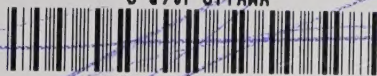


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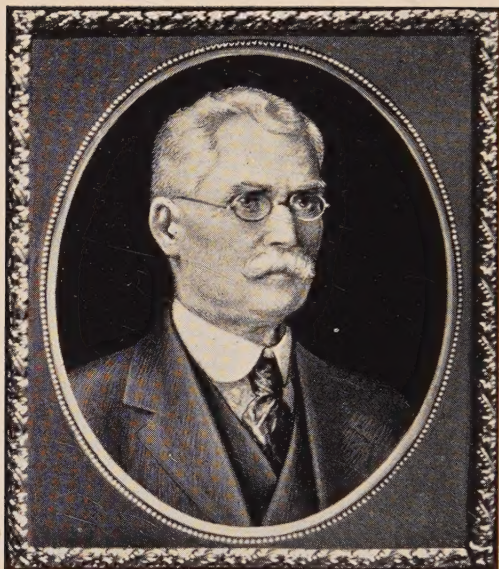


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A NEW VIEW OF
SURFACE FORCES



WILSON TAYLOR

1861-1923

FROM A MINIATURE BY HIS DAUGHTER

KATE LIVINGSTON CUMMING

A NEW VIEW
OF
SURFACE FORCES

A COLLECTION OF THE SCIENTIFIC PAPERS
OF
WILSON TAYLOR, B.A.

LATE OF THE
UNIVERSITY OF TORONTO

FORMERLY MATHEMATICAL MASTER IN THE COLLEGIATE INSTITUTES OF
STRATFORD, CHATHAM, PETERBOROUGH AND ST. CATHARINES, ONTARIO

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A MEMORIAL VOLUME

TORONTO
THE UNIVERSITY OF TORONTO PRESS
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PREFACE

WHEN Wilson Taylor died, on October 3rd, 1923, after spending four years in experimental research in physics, he left behind him a number of scientific papers. Lt.-Col. R. W. Leonard, who had made it possible, during the latter three years, for Mr. Taylor to carry forward his investigations, expressed a desire that a committee should examine the papers to determine if they were worthy of being gathered together and published.

The matter was referred to the undersigned, who, while not wishing to commit themselves to all the views propounded by Mr. Taylor, decided that the papers constituted a commendable contribution to science, well worth preserving in permanent form.

C. A. CHANT, *Convener*,
E. F. BURTON,
O. W. ELLIS,
H. E. T. HAULTAIN.

University of Toronto,
April, 1925.

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LIFE OF WILSON TAYLOR

Wilson Taylor was the son of James Taylor who was the son of Jasper Taylor.

Jasper Taylor came to Ontario from England in 1842 and settled on a hundred-acre farm near St. Williams in Norfolk County. The land was rough and wooded and the soil was light and poor, yielding a meagre return for the labour expended upon it.

At the time his father came to Canada James Taylor was nine years old. When he grew to manhood he married Matilda Montrose, whose family, originally from Scotland, came to Canada as United Empire Loyalists about 1790 and settled near Port Rowan, which is three and one half miles from St. Williams.

On January 16th, 1861, Wilson Taylor was born on the original farm. In 1875, when the boy was fourteen, his father was severely injured while felling a tree. Ever afterwards, until his death in 1894, he had to use crutches and while he could do gardening he could not work the farm. It thus fell upon Wilson to support his father, mother and four young sisters. He manfully undertook it but the burden was too heavy for his young shoulders and within a year the farm was sold for debt. The boy then worked as a farm labourer during the summer for several years, and through his work, for meagre pay, the family was able to exist.

In 1878 his mother died. The early introduction to the hardships of life implanted in him the sturdy independence of thought and action which was one of his chief characteristics in after life.

Until he was old enough to work, and during some winters when there was no work for him, he attended the country school and learned to read. One day in the autumn of 1879, while he was working in the field husking

corn, a neighbour driving by stopped and called over to him, "Are you going to school this winter, Wilson?" The lad had not thought of it before, but when he went home he picked up the dictionary to see how much he could read. When he found that he could understand what he read and could remember it, he decided he would go to school.

Next summer (1880) he passed the High School entrance examination and in January he entered the Aylmer High School. During the session both the headmaster and his assistant resigned and then a remarkable thing happened. The students presented a petition to the School Board asking that Mr. Taylor be put temporarily in charge of the school, which was done. His standing in the school is indicated by this fact. The new headmaster, chosen in the spring, was Francis Walter Merchant, who since then has had a distinguished career in the field of education in Ontario. He became principal of several of our largest Collegiate Institutes, then principal of a Normal School, then Director of Technical and Industrial Education and is now Chief Director of Education for Ontario. His high ambition and forceful character had a powerful influence on Wilson Taylor who obtained his non-professional certificate at the July examinations, 1881, and entered the Model School in the autumn.

For the first half of 1882 Mr. Taylor taught a country public school and in the autumn he transferred to Bothwell Public School, where he remained two and one half years. Desiring to improve his standing, in January 1884 he became a pupil of Ingersoll High School, of which Mr. Merchant was then Principal. He took an exceptionally difficult course during the term from January to July, covering the subjects both for First Class Grade C and First Class Grade A in Mathematics. The former included a general course in English, Mathematics, History and Science, of a standard at least as high as that required for an Upper School certificate at the present time. The latter included a course in Mechanics and Mathematics covering the honour work of the first year in the University and a good part of the honour work of the second year. Those who remember the examinations of

those days know that the standard maintained was exceptionally high, and very few reached it. Mr. Taylor passed both examinations in July 1884. Dr. J. A. McLellan, one of the examiners, stated that Mr. Taylor attained the highest standing ever reached at these examinations—over ninety per cent. on the average.

He then attended the autumn term of the Normal School at Toronto, in order to obtain a professional second class teachers' certificate, and at the end of the session he was awarded the Governor-General's Gold Medal for proficiency in teaching.

Mr. Taylor's health was never good, and as he had only the money which he earned and which he generously shared in the support of his father and sisters, it seemed impossible for him to attend the University or even to prepare for it.

In January 1885, on Mr. Merchant's recommendation, he was given a position on the staff of the Ingersoll High School where he remained for five years.

In July 1885 Mr. Taylor passed the professional examination for a first class teachers' certificate. It was at this time (July 1885) that the present writer met Mr. Taylor. During the summer vacation a school for instruction in elementary art was offered to teachers by the Department of Education. The present writer and Mr. Taylor had enrolled, and by chance had obtained lodgings in the same house. Mr. Merchant was one of the staff of the summer school, giving instruction in perspective. The session had hardly begun when Mr. Taylor learned that, unless he passed the professional examination for first class teachers that July, he would have to attend the Provincial School of Pedagogy, which had just been organized for the training of teachers who proposed to obtain positions in the high schools. The date of the examination was only ten days away. Mr. Taylor immediately gave up the art school work, bought or borrowed the prescribed texts on the theory, history and methods of education, some of them large volumes, and focussed all his powers upon them. He studied all day and much of the night, and passed the examination successfully.

On December 20th, 1886, Mr. Taylor married Nancy Livingston, a pupil at the Ingersoll High School. He still supported his invalid father and other members of his family.

Having now a home of his own, his health improved, and though he was qualified to teach in a High School or Collegiate Institute, he felt that his scholarship was not good enough for the highest positions in his chosen profession. He therefore began to study for the B.A. degree in the University of Toronto. Being mathematically inclined he chose the Honour Course known as Mathematics and Physics.

In May 1888 he went up for his first examination and obtained first-class honours. Those in first class honours in order of merit, were: 1. J. F. Howard, 2. R. Henderson, 3. W. Taylor, 4. G. F. Hull. Each one of the above has achieved distinction. Howard is Director of Mathematics for the Board of Education, San Antonio, Texas; Henderson, is 2nd Vice-President and Actuary of the Equitable Life Assurance Society of New York; Hull was a graduate student at the University of Chicago, where he obtained the Ph.D. degree, and for over twenty-five years has been Professor of Physics at Dartmouth College. With Nichols he made a famous research on the pressure due to light, and during the war he made valuable contributions to the solution of scientific military problems.

Though busily engaged in teaching Mr. Taylor found time to read the mathematical texts required, and next year, in May 1889, he passed the second examination, again obtaining third place in first class, the order now being: Henderson, Howard, Taylor, Hull.

He taught from September to the end of the year, but as in his course he was required to undertake some laboratory work, he resigned his position and in January 1890 attended the University. He remained until May, when he wrote his third examination, again obtaining first class honours, the order now being: R. Henderson, W. Taylor, M. Currie, J. F. Howard. Currie afterwards took an excellent course in medicine and located at his old home town, Picton. Later

he was elected to the Ontario Legislature, and to the House of Commons. Hull had dropped out temporarily to engage in teaching.

It was on the evening of February 14th, during the term when Mr. Taylor was in attendance, that the disastrous fire in the University occurred. Indeed just two days before it he was working in the Optical Laboratory, which was upstairs in the "Round Room" at the extreme end of the west wing. Being busily engaged, the time passed quickly and when he descended the stairs he found the door locked. He was unable to attract the attention of anyone and at last had to break a panel in the door through which he escaped. He reported what he had done to the authorities and was readily excused.

Mr. Taylor had hoped to return to the University to spend the fourth year in attendance, but his money was all gone, and being invited to take the position of Mathematical Master in the Stratford Collegiate Institute, of which Mr. Merchant was Principal, he began work there in September 1890. He remained until the summer of 1893. Mr. C. A. Mayberry, who was a member of the staff then and who has been the Principal of the Institute since January 1891, thus refers to Mr. Taylor's work:

"He was a remarkable mathematical scholar and very thorough in his teaching. While with us and during his previous teaching experience Mr. Taylor made a splendid reputation. I think it would be quite within the truth to say that no teacher in the Province had a better standing as a mathematical master. In addition to his high scholarship and his natural aptitude for teaching, Mr. Taylor was a man of fine character and devoted himself to his work with unusual care and enthusiasm. He was a hard worker and conscientious in all the details of his department. His chief characteristic was the one I have mentioned above—his thoroughness. It was impossible for a student to go through Mr. Taylor's classes in a slipshod or careless manner. He was an exact thinker himself and this habit it was his chief aim to instil in the minds of his pupils."

Similar testimony is borne by other colleagues. Mr. W. Briden, who was Principal of Ingersoll Collegiate Institute while Mr. Taylor was there, says:

"During the years of our association in Ingersoll I came to know Mr. Taylor intimately and to appreciate highly his noble qualities as a teacher

and as a man. His skill and ability in teaching were of a very high order. Possessing a thorough knowledge of mathematics, original in his methods and enthusiastic in his work, he inspired in his pupils high ideals of character, scholarship and work. As a disciplinarian he was tactful, sympathetic and firm rather than stern and severe, and he gained the admiration and respect of his students."

Mr. W. J. Twohey, of Chatham, and Mr. A. E. Coombs, of St. Catharines speak in almost the same words, which need not be quoted here.

Mr. Taylor's work at Stratford was very engrossing and he found it necessary to spend two years in his preparation for his final examination at the University. Indeed it is surprising that, in the midst of heavy teaching duties, he had been able to prepare for the previous examinations year by year and be able to take a stand with the very best in the class. In May 1892 he passed the B.A. examination, as usual attaining first-class honours, but the candidates were not ranked in order of merit.

In September 1893, then at the height of his powers, he entered Chatham Collegiate Institute as Mathematical Master, and he remained there until January 31st, 1913. He was already widely known as a teacher of mathematics but his reputation was greatly enhanced by the brilliancy of his work during the twenty years which he spent here. Many who received instruction from him secured high honours in his department, and they are the best witnesses to his skill and efficiency as an instructor. With boys who had a natural bent for mathematics Mr. Taylor was at his best. To them he gave inspiration and guidance.

One characteristic of his instruction was his attempt to get down to fundamental principles and to present the subject in a rigidly logical way. In attempting to carry out his views, he prepared an *Elementary Arithmetic* for use in the public and model schools of Ontario, which was printed in 1898. In view of the somewhat "reduced" condition in which Arithmetic is found in our schools at the present time, it will be interesting to quote some portions of the Preface, which is written in lucid style and clearly outlines the author's views.

The author says:

Probably no subject of study in our schools is of more educational value than arithmetic. More than any other it requires the student to form an accurate idea as to the magnitude of a quantity; to conceive the exact relation between the magnitudes of two quantities; by comparing two relations among three quantities, to obtain the necessary third relation by an act of the mind; and, finally, by repeating these processes under varying conditions, to bring a number of seemingly disconnected facts into relation, all tending towards a certain desired end. This on a small scale is just what the pupil must do on a large scale when he enters in earnest upon the practical affairs of life.

After giving what he considers to be the reason for some of the unsatisfactory results from the teaching of arithmetic, namely, through misconceptions regarding the meaning of "numbers", he states that he aims:

To clear up these misconceptions by enquiring into the origin and use of numbers; to lay down those principles which are at the foundation of all knowledge of number; and to build upon these fundamental principles the beautiful and useful science of arithmetic.

As might have been suspected, the book was cast in a somewhat too "philosophical" mould either for teachers or pupils. To his favourite pupils, its author no doubt presented the subject in a brilliant and enlightening way; but to most pupils, and indeed to many teachers, the subject of arithmetic must always be of a mechanical nature and disquisitions on the logic of the subject are simply wasted upon them. At any rate the work failed to secure authorization by the Department of Education, much to Mr. Taylor's disappointment.

In 1910 Mr. Taylor's eldest son John Wilson passed the honour matriculation examination, standing second in the Province in general proficiency, and in the autumn entered the University of Toronto. He graduated with honours in classics in 1914, took the M.A. degree in 1916 and the Ph.D. degree in classics at the University of Chicago in 1920. In 1912 his youngest son, Ross Malcolm, won the Prince of Wales Scholarship (the highest award) at matriculation; and Alfred Livingston, his second son, stood fourth in general proficiency and ranked for several scholarships. His daughter Kate Livingston had shown decided talent for drawing,

modelling and painting and had studied in Chatham, Detroit and Buffalo.

In the summer of 1912 the family moved to Toronto, in order that the three sons might attend the University and the daughter the Ontario College of Art, from which she obtained the degree of Associate in 1916. Mr. Taylor himself returned to Chatham in the autumn and remained until the end of January, when he accepted the position of Mathematical Master of the Peterborough Collegiate Institute. Here he remained for one and one half years, and during this time (at Easter 1914) he underwent a serious operation. In September 1914 he accepted the position of Mathematical Master of the St. Catharines Collegiate Institute, where he remained until 1920. In these years he underwent two more serious operations, and also suffered cruel losses in the Great War.

At the outbreak of the war his three sons volunteered for active service. John and Fred were rejected as physically unfit, while the youngest son, Ross, the very apple of his father's eye, was accepted on January 7th, 1915, being among the first group of students from Victoria College to enlist and the first of them to give his life. He joined the ammunition column of the 4th Brigade as bombardier and afterwards became despatch rider in the 13th Battery in France. While making his first round in the observation trench he was killed by a high explosive German shell on the afternoon of January 8th, 1916. He was a young man of the highest type, physically, mentally and morally.

Alfred Livingston was of the same calibre as his younger brother, and as the war was proceeding he made seven futile attempts to enlist, but was rejected because of defective eyesight. After the death of his brother he tried again and was accepted by the 182nd Battalion of Ontario County. He went overseas with the 116th Battalion in July 1916, and reached France in March 1917, in time to take part in the operations around Lens during that year. He had received his B.A. degree in May 1916, and in the winter of 1917-18 he represented the Khaki University at Vimy Ridge in the

116th Battalion. After a fortnight's leave in England, he returned to duty in France on August 15th and took part with the Canadians on the Hindenburg Line and met his death on August 28th, 1918.

The loss of these two promising sons was a terrible blow to Mr. Taylor—as well as to the rest of the family. For some time after their deaths their equipment and the letters which they had written continued to come to him, and it was months before the father could bring himself to open the letters.

It was in May 1919 that Mr. Taylor came upon his “new idea” as he expressed it. He was teaching the subject of surface tension to his senior class in the St. Catharines Collegiate Institute. As is well known, when a drop of water is divided into two other drops the area of the surface of the two drops is greater than that of the original drop and hence their joint potential surface energy is greater. If each of these two drops is again divided into two others there will be a further increase in the surface energy. What will happen if this division continues until the drop is reduced to its molecular units? The liquid drop will be turned into steam, and the potential energy it now possesses must be the heat of vaporization or the latent heat of steam. Working from this view Mr. Taylor was able to calculate the number and size of the molecules in water and in other substances.

Developing this principle, he prepared a paper containing his results and brought it to Toronto to ask some of his University friends to examine it. The view was expressed that it was new and valuable.

Feeling that he had made a discovery of a fundamental nature and of scientific value, he was anxious to undertake researches in surface tension and molecular physics, and sought assistance to enable him to carry out his investigations and to prove them to be of a practical nature. He obtained from the Honorary Advisory Council for Scientific and Industrial Research a grant of \$500 to enable him to engage a substitute at St. Catharines for two months.

He concentrated upon his investigations, and made considerable progress in opening up new avenues of work, but, as every one knows who has tried it, one can only make a beginning on a research in two months, and at the end of the time Mr. Taylor found the region of science which he was attempting to explore lay mostly unexamined before him. A small supplementary grant was secured to enable him to continue a little longer, and then it seemed he would have to return to his old post at St. Catharines.

But one chilly morning while waiting at the railway station at St. Catharines for the train for Toronto, which was a little late, he entered into conversation with another St. Catharines citizen who was also bound for Toronto. This was Lt.-Col. R. W. Leonard, a graduate of the Royal Military College, Kingston, and a prominent mining engineer and mine owner. Mr. Taylor, who was enthusiastic over his new work, naturally spoke of it to Col. Leonard. Now in the Coniagas mine at Cobalt, in which Col. Leonard had a large interest, the flotation process was used in recovering the metals, and so he was interested at once in the subject of surface tension. So he encouraged Mr. Taylor to describe his work, and when he found that the investigation was likely to cease through lack of funds he offered to support Mr. Taylor from his private purse. Thus, to his great joy, Mr. Taylor was allowed to proceed, and he simply lived with his researches until the day of his death.

The original paper which Mr. Taylor had prepared was carefully revised and improved and was published in the *Philosophical Magazine* in London, in June 1921, under the title "The Coalescence of Liquid Spheres; Molecular Diameters."

Many experiments on surface tension and molecular attraction were performed by Mr. Taylor, usually with simple apparatus of his own construction, and various papers embodying his results were prepared. One of these, entitled, "The Structure and Disintegration of Liquid Films" was published (in French) in *Annales de Physique*, January-February 1924. These papers are mostly extensions of

portions of his first one and the explanations of the various phenomena are based on the hypothesis that there is an "area-force" acting about liquid drops, even when they are reduced to molecular dimensions. This Mr. Taylor claimed to be of a fundamental nature, much as the law of gravitational attraction is of a fundamental nature.

While observing the way in which all liquids rush into small capillary openings the idea that this action might be used in the problem of preventing hardwood logs from sinking while being transported by water occurred to him. He thought that by heating the end of the log, hot melted paraffin would run into the capillary pores and when it became cold it would cork them up and prevent the water from entering and water-soaking the log. He made long and careful experiments on the length of time that logs of various woods would remain floating when treated in this way and amassed sufficient information to assure himself that his method could be applied successfully in the practical problem of the lumberman. He obtained patents for the process in Canada and the United States and constructed with his own hands a suitable heater and blower to apply the paraffin. He interested a number of lumbermen and also the Ontario Government in the process, and in several places made practical demonstrations of the method. At the very time of his death he had made an engagement to go down to Quebec to demonstrate his process. There is little doubt that if Mr. Taylor had been spared to carry out the method himself, or to have it done under his immediate direction, the process would have been shown to be practicable and commercially successful. He had high hopes that he would be able to make a valuable contribution to the lumbering industry and that he would reap some financial return from the process with which he could repay his generous benefactor. But he was the indispensable agent in carrying out the project and no one has yet appeared with the requisite ability, good judgment and scientific devotion to make the process a success.

Mr. Taylor was a man of many and varied talents. As

has been shown, he was a mathematician of exceptional ability; Dr. Merchant has told the present writer that in all his long experience he never had another student who approached Mr. Taylor in natural ability in mathematics—that, indeed, Mr. Taylor was in a class by himself. But he was also well read and had a fine appreciation of literature. He was also an expert mechanic. If a piece of apparatus was required for any purpose he could design it effectively and then construct it with great skill. Indeed he had abundance of natural ability. In the Collegiate Institutes at Stratford, Chatham and St. Catharines he installed programme clocks of his own design which rang the gongs efficiently for assembling or dismissing the classes according to time-table. Again, he had good ability as an artist. He was an excellent draughtsman and many of the diagrams in this book are precisely as he drew them. With his pen-knife he could make the most artistic carvings. In his home he had a handsomely carved case containing the medals and decorations won by his children.

Few people have stronger religious convictions than Mr. Taylor had and his faith was almost as simple as that of a child. He considered his meeting with Col. Leonard as directly due to the goodness of Providence, and no person could have felt more fully the responsibility of utilizing faithfully the opportunity given him to prosecute his researches.

While in Chatham Mr. Taylor became a competent accountant and was employed to audit the accounts of the city, his church and some business firms. He also took an active interest in the social and religious welfare of the community. He was a capable superintendent of the Sunday School of the Methodist Church in Ingersoll, and having considerable musical ability, he was a successful choir leader for a time. He also taught his boys to understand and appreciate music. As in everything else, he got down to the fundamentals in this subject too. After he had taught all he knew, the pupils were turned over to a competent teacher of music for a few terms. As a result they were

more proficient than many pupils after a long series of lessons and much practising. He believed in teaching music in the holidays rather than during the school term when there was so much work to be done.

He encouraged his boys in out-door play, but he always had a constructive object before him and he sought to teach them what would be useful in after life. He would take long walks with his children and would instruct them regarding the trees and other wonderful things to be seen in the woods, and he would impress upon them the mystery of all living things. In all this work, as well as in his later years of research, Mr. Taylor had the perfect sympathy and active support of his wife. It was not surprising that all the members of his family who grew to maturity (a son died at the age of three) showed exceptional intellectual ability and ambition to excel.

"Grim earnestness of purpose" and "stern sense of duty" are two phrases used in an appreciative editorial which appeared in *The Chatham Daily News* of October 9th, 1923, just after Mr. Taylor's remains had been interred at Chatham. These traits of character he endeavoured to transfer to all those about him—including, of course, his boys—and following out such teaching the two brilliant youths rushed to the colours and gave their lives in France. It was a severe test of his Christian character to treat with continued patience some of his frivolous pupils who had little taste for mathematics and no sense of responsibility, and some of the thoughtless ones did not at the time appreciate his kindly purposes. "But", to quote from the editorial referred to, "time, with maturity, brings to a young generation growing old a juster judgment; and to-day the thought that Wilson Taylor has passed on brings regret where he himself might least have looked for it".

Numerous incidents might be quoted to illustrate Mr. Taylor's sturdy independence of character and his refusal to accept a judgment which he felt to be unjust, but only one will be given.

On one occasion Mr. Taylor thought that the amount which was to be taxed against him when a cement walk was

to be laid before his property was far too high, and he protested vigorously. Further, he announced that he would construct it himself. So with the help of the boys the work was done—undoubtedly better than the Corporation would have done it and at one-fifth the outlay.

Mr. Taylor's health had not been good for a long time. For years he did not enjoy a full night's rest, but would waken in early morning with severe pains in his body. But by conserving his strength he devoted himself assiduously to his duties. Latterly, when living in Toronto, he placed his bed in his study so that every available minute might be given to his research. In 1919, two years after his operations in St. Catharines, his physician warned him that he could expect to live only two years longer; but by being careful every day and resting whenever he felt he should do so the two years were extended to four, and in that period he accomplished a remarkable amount of scientific experimenting and elaboration of his results.

When we see this man, after spending thirty-seven years in the exhausting task of instructing pupils of all ages and in continually impressing on them his high ideals of duty, embark upon original research and produce such a body of work in four years of fragile health, we cannot but admire his powerful mind and indomitable courage. If thirty years before, when he had graduated from the University, his steps had been directed into the paths of research he would undoubtedly have achieved high distinction in the world of science.

From an obscure corner in one of our great daily newspapers Mrs. Taylor rescued the following little poem by Alexander Louis Fraser; and those who knew Wilson Taylor intimately will agree that it may very appropriately supplement this biographical sketch.

C.A.C.

A QUESTION

"What did he leave?" men asked when he was gone.
Riches he did not leave, for he had none.
He left the world his work; his friends, a name
That ne'er shall be assailed by Spite or Blame.
"What did he take?" a question that is rare.
He took as much as any millionaire,
A soul unbartered for mere earthly things,
A treasure that outlasts the crown of kings!

ALEXANDER LOUIS FRASER

ARTICLE I

THE COALESCENCE OF LIQUID SPHERES— MOLECULAR DIAMETERS¹

Molecular phenomena are commonly considered as being caused by some kind of attraction which molecules have for each other when they are near together. This idea has been the basis for the explanation of such phenomena as the liquefaction of gases where the molecules near to each other are attracted so powerfully that they remain permanently in an aggregation. The idea was probably first suggested by Newton, and Laplace pointed out that the phenomena of surface-tension would result from the necessity for this attraction being unequally distributed among the molecules near the surface of the liquid. But he had to assume that this attraction ceased to be effective when the distance between the molecules was beyond a certain range. This has also been made the basis for the explanation of adhesion and solidification. Maxwell carried out Laplace's idea further, using it as a mathematical basis for the properties of the film in a soap-bubble. But difficulty was found in accounting for the formation of the black spots and the sudden changes in the tension of liquid films noticed by Rücker and Reinold in 1886. In recent years, however, the constitution of soap and other films has been studied in great detail, and some doubt has been expressed by various investigators as to the validity of the explanations which are based on the attraction of molecules as masses. From direct observation the soap-bubble appears to be composed of a number of strata whose multiples differ in thickness by steps which have been estimated to be from 1 to 10μ . The difficulty of explaining this by the attraction of molecules, or by any other hypothesis, has been so great that Perrin, who has made an exhaustive study of the bubble (*Annales de Physique*, Sept. 1918), speaks of it as an enigma.

This difficulty led the writer to study the action of two spheres of the same liquid when near to each other and when

¹From the *Philosophical Magazine*, Vol. xli, June 1921.

they came into contact; and the following may be considered as an attempt to consider an alternative basis for the explanation of molecular phenomena.

There was found no direct evidence that such spheres attracted each other, no matter how small they were down to microscopic dimensions, nor how closely they approached each other so long as they did not touch. But when contact was made a powerful force instantly came into play that caused the two masses to coalesce and become one sphere. This was found to be the case with all liquids, independently of the relative sizes of the spheres, and at all temperatures of the liquids. With mercury the action was instantaneous and very powerful. Sometimes, however, two or more mercury spheres would apparently lie in contact without coalescing, but on examination with the microscope it was always found that some foreign substance had accumulated on their surfaces and prevented their coming into contact. The question arose: Is it not possible that the same enveloping force which causes visible spheres to coalesce also causes the free molecules of a gas to come together into liquid aggregates?

Now, in any self-contained system of material masses any change in energy is from potential energy, either directly or through kinetic energy of large masses, into kinetic energy of the molecules of the system, that is, into heat. For to produce any change the forces of the system must become statically unbalanced, so that the resultant force does work against the inertia of large and small masses causing them to acquire kinetic energy.

It has long been observed that in many respects surface-tension appears to act as though it were something of the nature of an elastic envelope about a liquid mass trying to compress the mass into a smaller volume by contracting the area of the envelope. This tendency to change the volume, however, is due solely to the curvature of the enveloping surface, which tends to cause compression on the concave side and expansion of volume on the convex side. If there is no curvature there is no tendency either way to alter the

volume. The fundamental nature of the tension, then, is to tend to decrease the area of the surface.

Let us consider a system of three spheres of water whose diameters are .3, .4, and .5 cm. The potential surface energy of the system is $T \times \pi \{ (.3)^2 + (.4)^2 + (.5)^2 \}$, or $.50\pi T$ ergs. If these spheres be brought into contact, they will coalesce into one sphere whose diameter is .6 cm., and whose potential surface energy is $T \times \pi (.6)^2$, or $.36\pi T$ ergs. The potential surface energy which has been transformed into heat by coalescence is, therefore, $.14\pi T$ ergs. If we take, according to the best available data, $T = 73.3$ dynes per cm. at 15°C. , this energy amounts to 7.71×10^{-7} calorie, where $J = 4.184 \times 10^7$.

In the same way, if a large number of liquid spheres coalesce into a given mass, the heat produced would be considerable.

Let n = the number of these liquid spheres in a gram molecule,

d = the diameter of each sphere,

D = the diameter of the liquid gram molecule sphere,

m = the molecular weight,

ρ_θ = the density of the liquid at $\theta^\circ \text{A}$,

T_θ = the tension of the envelope about the liquid spheres at $\theta^\circ \text{A}$,

and L = the latent heat in calories of a gram mass of the gas at the boiling point.

Equating the masses before and after coalescence, we have

$$n \cdot \frac{\pi}{6} \cdot d^3 = \frac{\pi}{6} \cdot D^3,$$

from which

$$d = D \cdot n^{-\frac{1}{3}}.$$

Also, the potential surface energy has been reduced by coalescence from $T \cdot n\pi d^2$ to $T \cdot \pi D^2$. Therefore the amount which has been transformed into heat is $T \cdot \pi (nd^2 - D^2)$, which by the relation above may be written $T \cdot \pi D^2 (n^{\frac{2}{3}} - 1)$. Now, since n is very large in comparison with unity, $n^{\frac{2}{3}} - 1$ differs

but little from $n^{\frac{1}{3}}$, and thus this amount is $T \cdot \pi D^2 n^{\frac{1}{3}}$. Further,

$$\frac{\pi}{6} \cdot D^3 = \frac{m}{\rho}$$

and we see finally that the potential surface energy of the n liquid spheres which is converted into heat by their coalescence is $\left(\frac{36m^2\pi}{\rho^2}\right)^{\frac{1}{3}} \cdot T \cdot n^{\frac{1}{3}}$, a quantity which varies as the cube

root of the number of spheres obeying the law of coalescence, provided that T remains constant. This will be the case if the temperature remains constant, that is, if the heat is transferred to other masses such as the surrounding air and adjacent bodies.

Now, when a gram mass of a substance condenses from a gas into a liquid at the same temperature, there is produced L calories of heat energy which is known as the latent heat of condensation. Equating, therefore, these two amounts of energy, we have

$$T \cdot \left(\frac{36\pi m^2}{\rho^2}\right)^{\frac{1}{3}} \cdot n^{\frac{1}{3}} = mLJ,$$

from which

$$n = \left(\frac{LJ}{T}\right)^3 \times \frac{m\rho^2}{36\pi}.$$

The latent heat of evaporation is commonly thought to be the energy due to the attraction of molecules for one another at close ranges in the liquid. In the interior, where the attractions on a particular molecule are balanced, this energy is not apparent or is unavailable. It is apparent only in regions near the surface where these attractions are unequally distributed. The latent heat, then, is the work done in bringing the molecules of a gram mass from the interior through the surface region of unequal attraction and separating them from one another beyond the range of their attraction. Surface energy is regarded as the energy belonging to the molecules in the surface layer only, and, consequently, is only a part of the latent heat. Various attempts to define

the relation between latent heat and surface energy have so far been unsatisfactory; they assume the general form $EV^{\frac{2}{3}} = kL$ but the experimental data give no consistent values for the quantities involved. Other attempts to connect the whole internal molecular energy with the latent heat have failed for the same reason. These consist of seeking to verify relations of the form $N \cdot E_m = kL$, where E_m is the energy of one molecule and k is some constant.

A more successful attempt, however, was recently made "to give precision" to the generally recognized relationship between surface energy and internal latent heat by D. L. Hammick in an article on "Latent Heat and Surface Energy," which was published in the *Philosophical Magazine*, August 1919 and January 1920. He conceives the true molecular surface energy belonging to all the molecules in a gram molecule to be the potential energy they acquire in reaching their positions in the surface layer. He imagines the gram molecule spread out in a layer one molecular diameter in thickness on a surface of excess of the liquid. This energy is equal to EV/dJ calories, where E is the surface energy per sq. cm., d is the diameter of a molecule, and V is the volume of the liquid gram molecule. His argument to show that this surface energy is one-sixth of the internal latent heat is as follows. The work done upon a molecule to bring it into the surface layer is not, as is commonly supposed to be the case, one-half of that required to bring it altogether out of its liquid state. For, since the molecule in reaching the surface layer moves perpendicularly to the surface, the work is done against only "one of the three components of internal pressure," and is, therefore, only one-third of this amount, or one-sixth of the work to bring it altogether from the liquid.

It is difficult to conceive, however, that the work done by either of the other two components of internal pressure parallel with the surface can be equal to that done by the one perpendicular to the surface. For, in each of the former components, the forces which attract the molecule on opposite

sides are equal, and the energy is not available, since no work can be done by forces in equilibrium; whereas in the case of the latter component, the forces which attract the molecule towards the interior are greater than those which attract it towards the exterior, and the energy is available, since work may be done by their resultant. Still, from the best available data for d , E , and L for low temperatures, the calculated values of these two expressions for twenty-nine substances bear out his statement that "the relation above fits these facts remarkably well."

Another objection, which applies also to similar reasoning by other writers, lies in the division of the latent heat into two parts. If the external layer of molecules contains potential energy only equivalent to one-sixth of the latent heat, would not the other layers within the range of molecular attraction contain the remaining five-sixths and the surface energy be $6E$ ergs per sq. cm.? Or, is the latent heat composed of two distinct kinds, or does it arise from two distinct sources?

Now it so happens that Hammick's formula itself suggests a means of meeting completely both these objections. For his expression V/d for the area occupied by the molecules of a gram molecule when they are all arranged in the surface layer, assuming, as it does, that the molecules fill the whole volume, can be used to get the expression for the area occupied by one molecule. This area is $\pi d^3/6d$ or $\pi d^2/6$, which is exactly one-sixth of the area of its free surface. If, therefore, we suppose that the surface of the free molecule possesses surface energy of the same intensity as that which he supposes the surface layer to have acquired, the whole surface energy would be six times as much as Hammick thinks, and his relation should be:

$$E \cdot \frac{6V}{d} \cdot \frac{1}{J} = L,$$

which may evidently be written

$$E \cdot N \pi d^2 \cdot \frac{1}{J} = L_i,$$

where N is Avogadro's constant. Also, since his molecules occupy all the space in the liquid, we have

$$\frac{\pi}{6} \cdot d^3 = \frac{m}{\rho},$$

where ρ is taken at a low temperature. This enables his relation to be written:

$$E \cdot \left(\frac{36\pi m^2}{\rho^2} \right)^{\frac{1}{3}} \cdot N^{\frac{1}{3}} \cdot \frac{1}{J} = mL,$$

where $L_i = mL$, which is identical with that which we obtained by considering the surface energy given up by the coalescence of liquid spheres.

Thus the carefully compiled data supplied by Hammick's tables really account for the whole of the latent heat, and there is no need to employ the hypothesis of molecular attraction and the doubtful principle of equipartition of energy along the three geometrical axes to obtain a relation that fits in his experimental data.

In this connection it is interesting to note that Einstein (*Ann. d. Physik*, iv. 3, p. 513, 1901) has put forward a view that the surface energy of a liquid is of the nature of potential energy expressible by a certain equation, one of whose terms depends on the atomic weight. This is exactly what our formula does. The formula may be written

$$LJ = T \cdot \left(\frac{36\pi N}{m\rho^2} \right)^{\frac{1}{3}},$$

the expression with the brackets being the whole area of the N free molecules of a gram molecule of the gas, and T the energy per sq. cm. which we have supposed to exist in the surface of the free molecules. This energy is potential, as Einstein predicted, for it is stored in the surface of the free molecule incapable of being released for doing work until two such molecules by coming into contact coalesce and lessen their total enveloping area.

Our formula, which was obtained above from the phenomena of the coalescence of liquid spheres and not from any hypothesis concerning molecular attraction, would seem, then, to indicate that this view of the connection between the latent heat and surface energy is the correct one. We shall examine some further experimental evidences in support of this view.

If n , which on our view is Avogadro's number, is constant for all substances, we should seek for values of T and ρ which are independent of variable conditions of temperature, that is, for those values which they have when the temperature is $0^\circ A$. But, as Hammick points out, the data for these are not available, or at least are incomplete. The value of L , the latent heat at the boiling point, which is equivalent to the work done in dissociating the molecules from the liquid, that is, in creating the free surface of the molecules of the gas and storing it as potential surface energy, may be taken as constant under all conditions after our determinations have been freed from all external work.

Now, it has been shown experimentally that the surface tension about large masses of any liquid is a linear function of the absolute temperature which holds very approximately for all temperatures of the liquid from its melting point to the critical temperature θ_c . This result is expressed in the empirical formula

$$T_\theta = A + B\theta,$$

where A and B are constants for any particular liquid. For water the ordinary tables give $T_\theta = 0$ when $\theta = \theta_c = 638^\circ A$, and $T_\theta = 73.3$ as the best available value when $\theta = 288^\circ A$.

From these we have

$$T_\theta = 133.6 - .209\theta,$$

so that

$$T_0 = 133.6.$$

It is evident, however, that only in large spheres or masses can the tension of the envelope obey the law given above, for only in these can the heat motion of the molecules next the envelope affect the tension. For spheres containing only a few molecules and for the free molecules themselves an altogether

different condition exists, for the heat motion then is the motion of the sphere itself. The tension, therefore, of the envelope about the free molecule will be very approximately the tension about a large mass when the molecules are at rest, that is, the molecular tension T_m will be T_0 .

If, then, the law holds through the process of solidification and down to $0^\circ A$, we should have for the free water molecule $T_m = 133.6$. This seems to be a reasonable supposition when we remember that the forces which cause solidification are in the interior of the molecule or mass and would not, therefore, affect the tension of the envelope on the exterior of the molecule or mass. Moreover (see note at the end), there are experimental indications that the surfaces of solids possess potential energy and consequently are affected by surface tension.

Hence, if we take $L = 498$, which is the average of the values given in the tables corrected for external work amounting to 41 calories,

$$\rho_0 = \rho_{277} = 1, \quad m = 18, \quad \text{and} \quad T_m = 133.6,$$

the formula,

$$n = \left(\frac{L \cdot J}{T_m} \right)^3 \times \frac{m \rho_0^2}{36\pi},$$

gives by calculation²

$$n = 6.05 \times 10^{23}.$$

Millikan's value for this number, obtained by his balanced drop method, is 6.065×10^{23} ; while Perrin's value, obtained by studying the motion of a colloidal particle in water, is 6.86×10^{23} .

The result obtained above would seem to furnish an argument in favour of the view that the properties of surface tension can be considered as not depending upon the mutual attraction of molecules. For, if the free molecule has about it this elastic envelope, it is plain that the envelope cannot be material at all. It is simply a force and nothing more.

Since the force of gravity in its relation to potential

energy is denoted by $\frac{dE}{dx}$, where x is the distance between the centres of the masses attracting each other, this force will be denoted by $\frac{dE}{dA}$, where A is the area of the mass about which it acts. Also, because of the curvature of this area the force acts to compress the interior of the sphere to a smaller volume; but this action is prevented by another force in the interior which must, therefore, be denoted by $\frac{dE}{dV}$, where V is the volume within the enveloping force. It may be that all physical phenomena may be explained in terms of these three fundamental physical forces, of which beyond these distinguishing characteristics we know but little. What these forces are *per se* we have no idea.

The formula obtained above appears to hold for all spherical masses of liquids, whatever be their size. For, since it gives a value of N practically identical with those we already know, it suggests that the law of coalescence of water spheres does not break down at any point from the coalescence of large spheres to the coalescence of small spheres down to the molecules themselves. The method of obtaining it embodies in its essence discontinuity, involving from the beginning to the end no fewer than p distinct acts of coalescence where $2^p = \frac{N}{18}$, so that $p=75$.

At first thought it would seem that in the latter stages of condensation, where large spheres coalesce, the decrease in T on account of the heat motion of the molecules next the surface would greatly modify our value of N . Whatever effect this would have, however, must necessarily be very slight. For, suppose the first act of coalescence is to form the molecules into pairs, so that the resulting spheres each contain two molecules. Then, if we consider only a gram mass, the first act of coalescence may be proved to cause a transference of potential energy into heat amounting to $L(1-2^{-\frac{1}{2}})$ calories; the second act a transference of

$L(1-2^{-\frac{1}{3}})(2^{-\frac{1}{3}})$ calories; the third act of $L(1-2^{-\frac{1}{3}})(2^{-\frac{1}{3}})^2$ calories; and so on, the q th act of $L(1-2^{-\frac{1}{3}})(2^{-\frac{1}{3}})^{q-1}$ calories. These results are calculated in the table below.

TABLE I

q	Energy transferred
1	102.6 c.
2	81.4 c.
3	64.6 c.
4	51.2 c.
5	40.7 c.
..
21	1.0 c.
..
75 (final)	0.00000385 c.

At the completion of the fifth act the spheres each consist of 32 molecules, but the gram mass has suffered a change of potential surface energy into heat amounting to 340.5 calories, or of 68 per cent. of the whole. After the 21st act, which causes a change of only 1 calorie, the total surface energy remaining is only 3.91 calories, or considerably less than 1 per cent. Thus we see that the change in T on account of the heat motion in the large spheres towards the latter part of the process of condensation would not affect the value of N materially, but would cause only a slight increase.

Since the formula obtained above gives the value of N so closely approximating the true value from data experimentally determined in connection with water, we are led to think that the same value of N , though not to the same degree of approximation, would be obtained from similar data in connection with other substances which are chemically stable under the conditions involved in the determination of these data.

In the Tables II and III below are given the values of T_m and N , along with the necessary data, as calculated for ten of the more common substances, including water. L is the heat energy exclusive of that required for the external work necessary to vaporize a gram mass of the liquid at the boiling point without change of temperature under atmospheric pressure.

TABLE II

Substance	Formula	m	θ_c°	θ°	T_θ	$T_0 - B\theta$
Water.....	H ₂ O	18	638	288	73.3	133.6-.209 θ
Propyl alcohol...	C ₃ H ₈ O	60	536.7	288.4	23.8	49.5-.0925 θ
Ethyl alcohol...	C ₂ H ₆ O	46	516.1	293	22	50.9-.0986 θ
Methyl alcohol..	CH ₄ O	32	513	293	23	53.6-.105 θ
Ether.....	C ₄ H ₁₀ O	74	466.8	293	16.5	44.3-.095 θ
Chloroform.....	CHCl ₃	119.4	533	288	27.2	59.3-.111 θ
Nitrogen.....	N ₂	28	127	77	8.5	21.6-.170 θ
Oxygen.....	O ₂	32	155	90	13.1	30.4-.197 θ
Benzene.....	C ₆ H ₆	78	561.5	290.5	29.2	60.0-.107 θ
Mercury.....	Hg	200	(1734)*	290.5	547	657-.379 θ

*Theoretical.

TABLE III

Substance	Boil. Pt.	θ	ρ_θ	$T_m = T_0$	L	$N/10^{23}$
	°	°				
Water.....	373	277	1.000	133.6	498	6.05
Propyl alcohol....	370.2	293	.804	49.5	152	7.28
Ethyl alcohol.....	351.3	288	.794	50.9	192	10.09
Methyl alcohol....	337.7	288	.796	53.6	246	12.68
Ether.....	307.6	290	.718	44.3	73.4	1.13
Chloroform.....	334.2	273	1.526	59.3	52.4	1.24
Nitrogen.....	77	77	.79	21.6	41.0	.79
Oxygen.....	90	38	1.27	30.4	47.5	1.28
Benzene.....	353.2	378.4	.879	60.0	86.5	1.19
Mercury.....	629.7	0	(14.25)	657	61.6	.21

The temperature coefficient of surface tension has been assumed to be constant down to $0^\circ A$, and in accordance with the reasons given in the case of water we have regarded the surface tension T_m about a free molecule equal to T_0 in the empirical formula $T_\theta = T_0 - B\theta$. However, the temperature coefficient is only approximately constant, and consequently T_m or T_0 is only approximately determined. These data have been taken from the ordinary tables and are subject to question in some cases. Especially in the case of mercury, where L was determined by Young in 1910, there is a pro-

bability that the vapour of mercury involved in the determination was not altogether of dissociated molecules. For example, if the spheres of the mercury vapour contain 32 molecules, the real value of L is seen from Table I to be $498/(498-340.5)$ or 3.16 times the value in the Table III; and consequently the value of N would be

$$(3.16)^3 \times .21 \times 10^{23} \text{ or } 6.64 \times 10^{23},$$

which agrees with that we know.

But the greatest discrepancy is seen in the cases of ether, chloroform, nitrogen, oxygen, and benzene. The values of N , however, are very uniform and equal to about one-fifth of the true value. One contributing cause may be in the high vapour pressures common to all of these substances. But the chief cause lies in the use of ρ_θ instead of ρ_0 , which in the absence of sufficient data could not be estimated even approximately. So far as we have evidence, ρ_θ increases for the liquid quite rapidly as θ decreases, suddenly increases at solidification, and continues to increase more slowly for the solid down to $0^\circ A$. It seems to be quite possible that for these substances the value of ρ_0 would be double the value used; in which case, as N increases with the square of ρ_θ , the values of N would approximate to the true value. For mercury the value 14.25 for ρ_0 was obtained on the supposition that the temperature coefficient of expansion of the liquid remained constant through the solid down to $0^\circ A$.

In the case of the alcohols, from considerations in regard to the arrangement of the atoms in the molecule the idea has arisen that the free molecule is not spherical, especially as one of the elements is carbon. If this be so, two such molecules coming into contact would give up less of their enveloping area than they would if they were spherical and coalesced in the same manner as two liquid drops. At first they would resemble two solid particles adhering, and afterwards the combined mass would gradually become spherical as more molecules were included in the enclosure. It would, therefore, take a greater number of molecules in the initial stages of the condensation to produce the same amount of heat, which would account for the larger values of N for these

substances. Another cause may be the long ranges of temperature for which these substances are liquids.

It would appear, then, that the undetermined elements of these experimental data point to the idea that, if we knew the true values of T_m , ρ_0 , and L for all stable substances, the value of N calculated as indicated in our formula would be the true Avogadro's number, which would be a little greater than that obtained in the table for water. Also, the evidence from the data more carefully selected by Hammick points, under the same conditions and with the same limitations, to the same conclusion.

Assuming, therefore, that the conclusion is justifiable, we have, by equating the two expressions for the potential surface energy of the free molecule,

$$LJ \bigg/ \frac{N}{m} = T_m \times \pi d^2,$$

from which
$$d = \left(\frac{mLJ}{\pi T_m N} \right)^{\frac{1}{2}}.$$

This on substituting for LJ the value obtained previously reduces to

$$d = \left(\frac{6m}{\pi \rho_0 N} \right)^{\frac{1}{3}}.$$

The value of d will thus depend upon the value of ρ_0 and will be subject to the same uncertainty as that which belongs to ρ_0 . However, as ρ_θ is less than ρ_0 , d_θ will be larger than d_0 , so that d_θ may be regarded as the average diameter of the space which the actual molecule whose diameter is d_0 occupies at temperature $\theta^\circ A$. For water we are fairly certain that ρ_0 does not greatly exceed 1 and is not less than 1. The formula gives for water, where $\rho_0 = 1$, $d_0 = 3.85 \times 10^{-8}$. For mercury, where ρ_0 is taken equal to 14.25, $d_0 = 3.56 \times 10^{-8}$. As ρ_θ decreases with rising temperature, d_θ increases, thus making room for the heat vibrations of the real molecule in the solid or liquid.

The following is a brief summary of the views presented in the preceding pages:

(a) Latent heat is the surface energy of the free molecules of the substance in its gaseous state.

(b) Surface tension extends to molecular masses causing them to coalesce in the same manner as liquid spheres.

(c) Since N is constant for all substances, if any two of the three quantities T_m , ρ_0 , and L can be found for any substance, the other may be calculated from the relation

$$N = \left(\frac{LJ}{T_m} \right)^3 \times \frac{m\rho_0^2}{36\pi}.$$

(d) It is assumed that the empirical law $T_\theta = T_0 - B\theta$ holds down to $0^\circ A$, and that $T_m = T_0$.

(e) The actual mass diameter of the molecule is

$$d_0 = \left(\frac{6m}{\pi\rho_0 N} \right)^{\frac{1}{3}},$$

and the average diameter of the space it occupies in the solid or liquid is

$$d_\theta = \left(\frac{6m}{\pi\rho_0 N} \right)^{\frac{1}{3}}.$$

Note on the Surface Tension of Solid Bodies¹

The idea that solid bodies possess surface tension is believed to be tenable. Van der Mensbrugge (*Anal. Soc. Sci. de Bruxelles*, B. xxix, (1904-5)), from consideration of the forces in the curved meniscus at the side of a vertical glass plate in water, concludes that a glass surface possesses an effective surface tension. M. Petrova (*Jurn. Russk. Fizik. Chimecesk*, xxxvi, Phy. pt. pp. 203 (1905)), from the fact that enlarged photographs of mercury drops on glass taken before and after solidification when superimposed showed no appreciable change, inferred that solid mercury possesses surface tension. And, finally, M. Berggren (*Ann. d. Physik*, xlv, 1, pp. 61-80 (1914)), by measuring the velocity of deformation when amorphous bodies solidify in the case of threads hanging vertically, found that solid amorphous bodies possess surface tension of the same order of magnitude as that of liquids.

¹Vide Satterly: Trans. Roy. Soc. of Canada, 1922, Section III, page 83, for criticism of parts of this paper.

ARTICLE II

THE LAW OF COALESCENCE OF LIQUID SPHERES

I

Surface tension is recognized as a phenomenon of the free surfaces of liquids, of liquid interfaces, and of the surfaces of bubble films. It seems likewise to operate not only in connection with the free surfaces of solids and the interfaces between liquids and solids, but also with the bounding surfaces of free molecules. Surface tension is conceived, in fact, to act in the surface boundary separating mass and ether, or in the boundary where mass adds its properties to those of ether, whatever these may be. It is a force which may be measured in terms of its chief property, which is to lessen, or tend to lessen, the enveloping area about any free mass. It appears to be, like gravity, elemental in its nature. For, if it acts in the surface of the free molecule, it cannot be due to molecular attraction; nor, to the knowledge of the writer, has any evidence been adduced to show that it is the result of electrical forces.

Further, by virtue of this enveloping tension about its mass, the free molecule possesses in its surface a definite measurable amount of potential energy, P , depending on two constant quantities, the surface tension, T_m , and the diameter, d , such that

$$P = T_m \times \pi d^2.$$

This potential surface energy is thus quite distinct from the kinetic or heat energy, K , of the free molecule, which depends on its mass, M , and its velocity, v , such that

$$K = \frac{1}{2} M v^2.$$

Now, our formula¹

$$LJ = T. \left(\frac{36\pi N}{m\rho^2} \right)^{\frac{1}{3}},$$

which may be deduced from the Hammick formula, may be written

$$mLJ = N.T\pi d^2, \text{ since } d = \left(\frac{6m}{\pi\rho N} \right)^{\frac{1}{3}} = N.P.$$

¹Vide Article I, p. 27.

Consideration of the above shows that mLJ , the true latent heat of a gram molecule of a gas, is the sum of the potential surface energies, P , of the free molecules that compose it. Consequently,

$$P = mLJ/N.$$

We are thus able to determine the potential surface energy carried by each free molecule of a gas when the true latent heat has been measured. For any particular gas, it is a constant quantity independent of the temperature of the gas. On the other hand, the kinetic energy of the free molecule suffers a change every time the molecule comes into collision with another which differs in mass, or is moving with a different velocity, as when a molecule of a gas strikes a molecule in the side of the containing vessel. The aggregate of this energy, K , possessed by all the separate molecules of a gram mass is known as the absolute heat, and the change in it for each degree in temperature as the specific heat of the gram mass.

Heretofore it has not been thought necessary to make a distinction between the true latent heat, which is independent of temperature, and the specific heat, which depends on temperature, and we often find that the latent heat of the same substance is given for different temperatures. This, for example, is the case with Young's determinations, where for many substances he gives no determinations corresponding to the boiling points. In such cases the numbers involve, besides the true latent heat, a certain amount of specific heat and the external work done against the air pressure.* Ham-

*Thus for ethyl alcohol Young (*Physical and Chemical Constants*, Kaye & Laby, 1911, p. 61) does not give the latent heat at the boiling point, 78.3° C. When this is found by interpolation his results may be analysed as follows:

Temperature	Observed Lt. Ht.	True Lt. Ht.	Specific Heat	External Work
0° C.	220.9 cal.	=191.9 cal.	+17.2 cal.	+11.8 cal.
60° C.	213.4 "	=191.9 "	+ 7.1 "	+14.4 "
78° 3 C.	(207.0 ")	=191.9 "	+00.0 "	+15.1 "
80° C.	206.4 "	=191.9 "	- .3 "	+15.2 "
100° C.	197.1 "	=191.9 "	-11.9 "	+16.1 "

mick also confuses the two when he states that the latent heats for low temperatures are not available.

Before considering the relation between these two kinds of energy possessed by the free molecule, let us examine the natural processes by which two liquid spheres coalesce and one liquid mass is separated into two free liquid spheres.

(1) If two small glass spheres formed by fusion on the ends of two small straight steel wires which serve as handles be dipped into any liquid which "wets" the glass, or be brought into contact with free spheres of such liquid, the glass spheres are completely surrounded by the liquid. Each liquid mass, then, as far as its free surface action is concerned, will behave precisely in the same way as a free liquid sphere. These may be brought very close together and no movement is

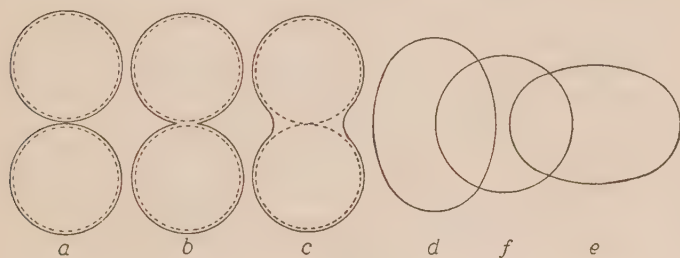


Figure 1.

observable. But, if contact is once made, a violent action immediately takes place, a neck is formed connecting the two liquid masses into one mass, and the whole is surrounded by one enveloping force that holds the two glass spheres firmly together. This is shown in Fig. 1 (a), (b), and (c), where the glass spheres are represented by dotted lines.

It would appear, then, that as soon as contact is made the areas in contact give up their potential surface energy, the enveloping forces unite at the circumference of the common area and cease to act in the area itself. An opening, as it were, is made, through which the two liquid masses are free to intermingle. The surface force in reducing the enveloping area rapidly draws in the sharp edge around the opening,

as seen in Fig. 1 (*b*), until a state is reached, as in Fig. 1 (*c*), when the whole mass is enclosed within a minimum area. If the glass spheres were absent, the enclosed mass would vibrate for a time with decreasing amplitude between a prolate spheroid, Fig. 1 (*d*), and an oblate spheroid, Fig. 1 (*e*), until it came to rest in a spherical form, Fig. 1 (*f*).

(2) If, now, the glass spheres be slowly separated, Fig. 2 (*b*), the liquid neck becomes narrower and longer. The curvature of the surface about the neck in any plane through its axis grows less, while the curvature in the plane through the normal perpendicular to this increases, until the latter greatly exceeds the former. By virtue of these curvatures the surface tension tends to enlarge the volume of the mass in the first

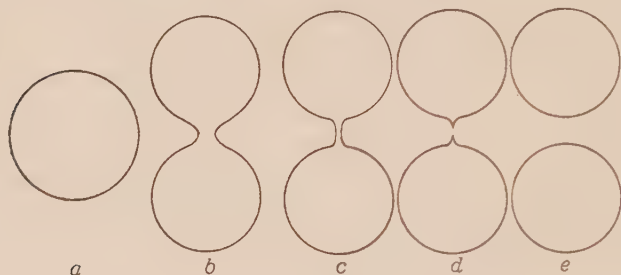


Figure 2

case and to lessen the volume of the mass in the second case. Since these tendencies to change the volume of the mass are proportional to the curvatures, the mass in the narrow part of the neck where the pressure is increasing will be driven in both directions to those regions where the pressure is less. There will, therefore, come a time when the last two molecules are at the point of separating. There is nothing to prevent the enclosed masses adjusting their form so that the separation is effected only when the neck is very small, and when the enveloping force having no mass between to prevent contact closes in upon itself and ceases to act. This separation of the spheres is brought about by the continuous application of external energy only so long as an increase of enveloping

area is required. At a certain stage, however, this external energy is no longer needed; for, after the neck has reached a certain length, which may be proved to be $9/4$ of its diameter, the enveloping area begins to decrease. From this stage the process goes on automatically. This is shown in Fig. 2 (c), (d), and (e). When large spheres of liquid are thus separated, it frequently happens that the flow of the liquid is not rapid enough for all of it to escape. The neck parts at two or more points and one or more small spheres are formed between the main ones. This is generally the case when one sphere of water is separated from another by gravity.

(3) When water is allowed to stand in a glass vessel, small air bubbles are formed which attach themselves to the glass under the water. One of these may be detached and carried through the water on a pin point until it comes into contact with another formed on the side of the vessel. The two then coalesce and the resulting bubble either remains attached to the glass or rises to the surface, where, after a short pause, it coalesces with the air above. In both of these cases of coalescence the contact takes place on the liquid or mass sides of the enveloping areas, and, as before, when the contact was on the ether sides, the contact areas yield up their potential surface energy as soon as the contact is made. The process is shown in Fig. 1, where the circles represent the air chambers and the space outside represents the liquid. The contact occurs when the last three molecules, by adjusting the form of their mass as it is pressed outwards from the central position, allow the areas to approach each other very closely before contact actually takes place.

From these observations it seems to be true that the enveloping force has a simple universal property which may be stated as follows:

Whenever two enveloping force areas come into contact, the areas in contact give up their potential surface energy, since the surface forces unite at the circumference of the common area and cease to act in that area.

Correlated to this is the principle that *at no time in the process of forming an aggregation of mass, or of separating an aggregation into parts, can there be a free surface in which the enveloping force does not act, and which does not possess potential surface energy.*

Now it has been shown in the previous paper that the law of coalescence of free liquid spheres also holds in the case of the free molecules of a gas. Consequently, the above properties are applicable to molecules as well.

It is possible to determine mathematically the relative value of the loss of potential surface energy when two unequal spheres of the same liquid coalesce. Referring to Fig. 1, let the diameters of the spheres be d and D , d being less than D , and let $d/D=r$. After coalescence, the diameter of the resulting sphere is $(d^3+D^3)^{\frac{1}{3}}$, and the loss in potential surface energy

$$\begin{aligned} &= T. \{ \pi d^2 + \pi D^2 - \pi (d^3 + D^3)^{\frac{2}{3}} \}, \\ &= T. \pi D^2 \left(r^2 - \frac{2}{3} r^3 + \frac{1}{9} r^4 - \frac{4}{81} r^5 + \text{etc.} \right), \\ &= T. \pi d^2 \left(1 - \frac{2}{3} r + \frac{1}{9} r^2 - \frac{4}{81} r^3 + \text{etc.} \right). \end{aligned}$$

Therefore the ratio which this loss bears to the potential energy carried by the larger sphere

$$= r^2 - \frac{2}{3} r^3 + \frac{1}{9} r^4 - \frac{4}{81} r^5 + \text{etc.},$$

and to that carried by the smaller sphere

$$= 1 - \frac{2}{3} r + \frac{1}{9} r^2 - \frac{4}{81} r^3 + \text{etc.}$$

Now, if r is very small, the former ratio vanishes and the latter becomes equal to unity. Hence, when either a small liquid sphere or a molecule enters a large liquid mass, it forfeits all its potential surface energy, without giving any to the larger mass. This, for example, is the case when a rain drop falls into a pond or a molecule enters a dew drop. Of course, the kinetic energy of the combined mass is increased. On the other hand, since no energy can be de-

stroyed, the amount of energy required to eject a molecule or small liquid sphere from a large mass must be exactly equal to the potential surface energy it carries afterwards. Thus the free molecules and mist particles of water which are in the air surrounding the earth hold in the form of potential surface energy the exact equivalent of the radiant energy of the sun expended in ejecting them from larger masses of water. In this form the heat from the sun is carried by the air currents over the land surface where, by coalescence of water particles, it is again freed and, in the form of heat, is effective in modifying the climate.

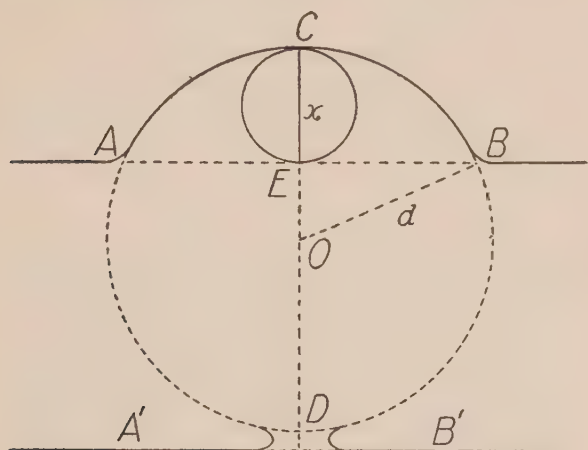


Figure 3

Likewise, when a molecule or liquid sphere is separated from a large liquid mass, the rate at which this heat energy is supplied, to be stored up as potential surface energy, may be mathematically determined.

In Fig. 3 the large circle ABD , whose centre is O , represents a molecule or small liquid sphere of diameter d emerging from the surface, AEB , of a mass of liquid, its vertex having reached a height $CE = x$ above the surface. Let a sphere be described on CE as diameter and let OB be joined. Then the energy required to cause the sphere to

emerge a distance x is equal to the difference between the potential surface energy belonging to the spherical cap ACB and that belonging to the plane circle AEB . If y denotes this energy, we have

$$\begin{aligned} y &= T(\pi dx - \pi BE^2) \\ &= T\pi(xd - OB^2 + OE^2) \\ &= T\pi\{xd - OB^2 + (OB - x)^2\} \\ &= T\pi x^2. \end{aligned}$$

Thus, the energy required to bring the sphere a distance x out of the liquid is exactly equal to the potential surface energy belonging to a liquid sphere, or to a hypothetical molecule, whose diameter in either case is the height of emergence above the surface. Consequently, the energy required to bring a molecule half way out of its liquid is only one-quarter* of the amount required to bring it all the way out, and half of this total amount will bring it $1/\sqrt{2}$ or $7/10$ of the way out.

Again, since $dy/dx = 2T\pi.x$, we should expect that the energy of ejection would have to be supplied at a rate that increased proportionally with the distance the sphere had emerged. But the formula assumes that there are sharp angles at A and B between the surfaces of the sphere and of the liquid, whereas in any observed case there is an actual curve connecting the two surfaces. It does not take account either of the formation of the neck at D connecting the separating sphere and the liquid below the surface $A'B'$, which allows the sphere to emerge a distance greater than the diameter before complete separation takes place. It does, however, apply very approximately throughout the whole process until the height of emergence approaches the value of d . Then the influence of the neck begins to modify the accelerated rate of the supply of energy. For values of x greater than d the formula, $y = T\pi x^2$, ceases to have any physical interpretation. For values approaching d the rate of the supply of energy is modified by another law altogether.

*Not one-half as is commonly assumed, or one-sixth as Hammick thinks. *Phil. Mag.*, Vol. 38, p. 240, 1919.

However, when complete separation is effected the formula does show the total energy supplied, which is $P = T\pi d^2$.

Now, we have seen that two free surfaces, becoming tangential, unite their forces at the circumference of the tangential area and cease to act in the area itself. The complete reversal of this process would be the splitting up in the interior of a mass of an area having no potential surface energy into two surfaces having potential surface energy. This cannot take place, just as gravity cannot be reversed in direction. Complete dissociation [see Fig. 2 (c) and (d)] can take place only when the tension force about the neck closes in upon itself between the separating masses of the last two molecules. These changes are approximately represented in Fig. 4 below; the energy supplied has been plotted against the height of emergence. The curve is a true parabola from O to A , at which point the influence of the neck begins to be felt. It then bends to the right and becomes horizontal at the point of separation, C , where $y = T\pi d^2$

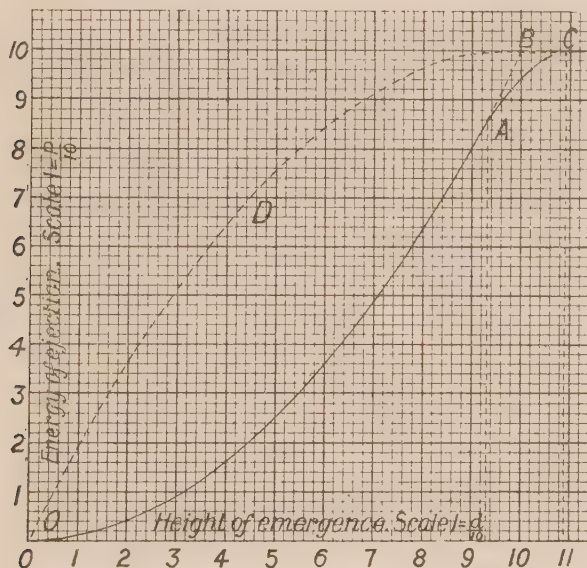


Figure 4.

and x is considerably greater than d . Were it not for the modification brought about by the formation of this neck, the parabolic curve would continue to the point B , where $x=d$, and then change suddenly to the horizontal direction. This abrupt change in direction at B corresponds to the instantaneous creation of two free surfaces in the interior mass which, as was shown above, cannot take place.

But when a molecule is entering a liquid, no energy is given up until there is actual contact, and then there is a sudden release of a large amount in the contact areas. This brings into play forces powerful enough to cause a visible wave shock to extend over a wide circular area when a small water sphere is carefully brought to touch the surface of a large mass in a vessel. The energy given up when a molecule or liquid sphere has entered to a distance x below the surface has been plotted also in Fig. 4, and the resulting dotted curve, ODB , is of the same form exactly as the unmodified parabola, OAB , but is reversed in position with the vertex at B .

The writer believes that this is the true nature of what is commonly known as molecular attraction. The range of action of the force, as in the case of two coalescing molecules, is really less than two molecular diameters, and the force itself is inconceivably more powerful than gravity. This may be inferred from the following calculations in connection with the water molecule.

(a) The binding force of this tension acting across the equator of the free molecule, which would be the same as that exerted by the enveloping force in the cylinder about two adjacent molecules to hold them together,

$$= T \cdot \pi d = 134 \times \pi \times 3.85 \times 10^{-8} = 1.61 \times 10^{-5} \text{ dynes.}$$

The gravitational attraction of their masses

$$\begin{aligned} &= G \times M^2 / d^2 = 6.658 \times 10^{-8} \times \left(\frac{18}{N} \right)^2 \times \left(\frac{1}{3.85 \times 10^{-8}} \right)^2 \\ &= 4.00 \times 10^{-38} \text{ dynes.} \end{aligned}$$

The pull, then, of the tension force around a molecule is 4.03×10^{32} times as great as their mutual gravitational attraction.

(b) Again, if two molecules as hemispheres compose one spherical aggregation, their centres of mass are at a distance $\frac{3}{8}d$ apart. Then the whole work done against their gravitational attraction in moving them to an infinite distance apart

$$= \int_{\frac{3}{8}d}^{\infty} F \cdot dx = G \cdot \left(\frac{18}{N}\right)^2 \int_{\frac{3}{8}d}^{\infty} \frac{dx}{x^2} = G \left(\frac{18}{N}\right)^2 \times \frac{1}{\frac{3}{8}d}$$

$$= 7.87 \times 10^{-45} \text{ ergs.}$$

But the work done against the enveloping force in separating the molecules from each other

$$= 134 \times (2 - 2^{\frac{3}{8}}) \pi d = 2.56 \times 10^{-13} \text{ ergs.}$$

Thus the energy required to separate the molecules against their enveloping force is 6.36×10^{31} times as much as that required to separate them against their gravitational attraction.

(c) Finally, by Laplace's formula, the pressure on the interior mass of a molecule due to the curvature of the enveloping force

$= 4T/d = 1.39 \times 10^{10}$ dynes, which is equivalent to a pressure of about 13,900 atmospheres,* or to the pressure of the sea at a depth of 84 miles.

These results show that for molecular distances and masses Newtonian gravitation has no appreciable effect in comparison with the effect of the enveloping forces of surface tension. The expression a/v^2 , which occurs in van der Waäl's equation,

$$(p + a/v^2)(v - b) = R\theta,$$

*In recent investigations into high pressures carried out in the Jefferson Laboratory of Harvard University, Dr. P. W. Bridgman found that when water was subjected to a pressure of 12,000 atmospheres inside a heavy steel cylinder its volume was decreased by 20 per cent. It would be interesting to know whether this was due to a decrease in intermolecular space or to a decrease in volume of the molecular mass itself. If the latter be the case the result given above would indicate that the mass of the free molecule has undergone considerable compression on its emergence from its liquid.

and which was deduced from the hypothesis of the existence of an attraction between molecular masses when close together, may have no actual relation to physical phenomena.† Physicists are not agreed as to the meaning to be ascribed to the quantity a . Some regard it as a constant, while others regard it as a function of the temperature. Hammick is undecided and treats it according to both meanings. Its success in accounting for certain experimental results is probably due to the nearness with which the accepted hypothesis of molecular attraction approximates the actual process of coalescence. The failure of the gas law, $PV=RT$, to hold when the gas is near the point of condensation seems to be due to some of the molecules with slow velocities coming into contact with each other and with the sides of the containing vessel and remaining permanently attached.

II

We have shown that the enveloping force for molecular distances and masses is incalculably greater than the force of gravitation and that it acts according to a simple and definite law. It remains to inquire into the conditions under which coalescing molecules are held in a permanent aggregation. The following is an attempt to investigate the problem from the point of view of the law of the enveloping force as stated in the former part of this paper.

Assuming that the conclusion of our previous article is correct, namely, that the heat energy required to dissociate completely the molecules of a liquid is precisely equal to the potential surface energy of the free molecules of the gas, we may, as has been seen, calculate the potential surface energy P , which belongs to one molecule, by dividing the true latent heat of a gram molecule of the gas by Avogadro's constant N . Thus,

$$P = mLJ/N,$$

where m is the molecular weight, L is the true latent heat, which is obtained by diminishing the observed latent heat of

†*Phil. Mag.*, V. 37, pp. 65-97, 1919, also V. 31, p. 22, 1916.

a gram mass by the work done against atmospheric pressure, $J = 4.184 \times 10^7$, and $N = 6.05 \times 10^{23}$. P , then, is a quantity independent of variations of temperature and pressure. Its magnitude is of the order of 10^{-14} ergs.

The accompanying Table I contains a list of 38 substances. From data available in standard tables the potential surface energy of the free molecule of each substance has been computed, except in the case of mercury (39), where P has been obtained from a theoretical value of L , 187, which, as was pointed out previously, it must have in order that our formula,

$$N = \left(\frac{LJ}{T} \right)^3 \times \frac{m\rho^2}{36\pi},$$

may give a consistent value of N .

In Table I is included a group of eight substances, Nos. 31 . . . 38, whose latent heats have been determined, chiefly by Young. On account of certain peculiar physical or chemical properties possessed by them their k/P values have not been considered sufficiently reliable to be included in the general average. In column 8 will be found, for each of the different substances, the kinetic energy of the free molecule of the substance in the gaseous state at the boiling point. In determining these values it was assumed that no condensation took place on the sides of the containing vessel, so that $R\theta$ is the heat energy of a gram molecule of the gas at the boiling point θ° A. Thus,

$$K = R\theta/N,$$

where

$$R = 8.315 \times 10^7.$$

K has the same order of magnitude as P . The ratio which the kinetic energy bears to the potential surface energy of the free molecule is given in column 9.

It might reasonably be expected that this ratio would have an important bearing upon the interchange of a substance between the liquid and gaseous states. A study of this column seems to confirm this view. For the thirty substances whose latent heats may be regarded as fairly accurate the ratios are approximately uniform, and show an average of slightly

TABLE I

No.	Name	Formula	m	$B.P.$	L	$P \times 10^{14}$	$K \times 10^{14}$	K/P
1	Nitrogen.....	N ₂	28	78	42.6	8.14	1.07	.131
2	Oxygen.....	O ₂	32	90	54.4	10.04	1.24	.124
3	Carbon Dioxide..	C O ₂	44	194	101	30.7	2.67	.0871
4	Ether.....	C ₂ H ₁₀ O	74	307.6	80.0	40.9	4.23	.106
5	Pentane.....	C ₅ H ₁₂	72	309	78	38.3	4.25	.111
6	Car. Disulphide..	C S ₂	76	319.2	75.4	39.5	4.39	.111
7	Ethyl Bromide..	C ₂ H ₅ Br	109	311.4	54	40.7	4.28	.105
8	Methyl Iodide...	C H ₃ I	142	315	42	42.1	4.33	.103
9	Methyl Formate..	C ₂ H ₄ O ₂	60	305	100.4	41.7	4.19	.100
10	Ethyl Formate..	C ₃ H ₆ O ₂	74	327	89	45.5	4.50	.099
11	Acetone.....	C ₃ H ₆ O	58	329	113.7	45.6	4.52	.099
12	Ethyl Iodide....	C ₂ H ₅ I	156	345	42.6	46.0	4.74	.103
13	C. Tetrachloride	C Cl ₄	154	350	40.5	48.0	4.81	.100
14	Ammonia.....	N H ₃	17	239.5	255	29.9	3.30	.110
15	Methyl Acetate..	C ₃ H ₆ O ₂	74	330	91	46.6	4.54	.098
16	Ethyl Acetate...	C ₄ H ₈ O ₂	88	350	78.5	47.8	4.81	.101
17	Benzene.....	C ₆ H ₆	78	353	84	45.3	4.85	.107
18	Toluene.....	C ₇ H ₈	92	394	75.7	48.2	5.28	.110
19	Propyl Acetate..	C ₆ H ₁₀ O ₂	102	375	66.4	46.8	5.14	.110
20	Ethyl Propionate	C ₅ H ₁₀ O ₂	102	373	71.7	50.6	5.13	.101
21	Chloroform....	C H Cl ₃	119	334	53	43.6	4.59	.105
22	Aniline.....	C ₆ H ₇ N	93	457	96.7	62.2	6.28	.101
23	Turpentine.....	C ₁₀ H ₁₆	136	432	67.7	63.7	5.94	.0933
24	Sulphur.....	S	32	589	325	71.9	8.09	.112
25	Mercury.....	Hg	200	630	59.7	82.6	8.66	.105
26	Amyl Alcohol...	C ₅ H ₁₂ O	88	404	111	67.5	5.55	.0822
27	Ethyl Alcohol...	C ₂ H ₆ O	46	351	195	62.0	4.81	.0776
28	Methyl Alcohol..	C H ₄ O	32	339	244	54.0	4.66	.0863
29	Propyl Alcohol..	C ₃ H ₈ O	60	370	152	63.1	5.09	.0807
30	Water	H ₂ O	18	373	498.5	62.2	5.13	.0814
	Average.....							.101
31	Hydrogen.....	H ₂	2	20.4	103	1.4	.28	.200
32	Chlorine.....	Cl	35.5	239.4	53.6	13.16	3.30	.251
33	Iodine.....	I	127	473	17	14.96	6.50	.434
34	Bromine.....	Br	80	334	37.3	20.6	4.57	.223
35	Phosphorus	P	31	561	94	20.1	7.70	.383
36	Sulphur Dioxide	S O ₂	64	263	86.2	56.2	3.62	.0664
37	Nitrous Oxide...	N ₂ O	44	183	127	39.6	2.50	.063
38	Acetic Acid.....	C ₂ H ₄ O ₂	60	391	72.6	30.1	6.75	.224
39	Mercury(Theor'l)	Hg	200	630	187	265	8.66	.0327

more than $1/10$. Thus we have a law which defines the boiling point of any liquid:

$$K/P = 1/10$$

Further, since $K = R\theta/N$, and $P = mLJ/N$, this equation may be reduced to the form

$$mL/\theta = 10.R/J, \text{ or } mL/\theta = 19.7.$$

That is, the ratio of the latent heat of a gram molecule of any gas to the boiling point on the absolute scale is a constant. This is known as Trouton's rule to which a physical meaning may now be given as follows:

A substance is a gas when the kinetic energy of its free molecule exceeds $1/10$ of its potential surface energy; it is a liquid when it falls short of this amount; and it is changing from one state to the other when these two amounts of energy are equal to each other. In other words, since $10.NK = NP$, a substance is a gas, a liquid, or is changing its state, according as ten times its absolute heat is greater than, less than, or equal to, the true latent heat of its gas.

A closer examination of this ratio, however, reveals some important exceptions which may necessitate a modification of this rule. For instance, the four alcohols and water, whose latent heats may reasonably be regarded as very accurately determined, give the ratio K/P uniformly less than the average and equal to about $1/12$, while mercury (39) gives a value of only $1/30$.

In the accompanying Fig. 5 (see the next page for figure), K has been plotted as ordinate against P for the 38 substances. It will be seen that the points corresponding to the first thirty of the substances group themselves fairly along the straight line OA which, therefore, represents Trouton's rule. The four alcohols and water form a group by themselves at some distance to the right of the line, while mercury (39) gives a point very far to the right. Hydrogen, nitrogen, and oxygen give points which are near the origin to the left. The remaining eight substances, (31) . . . (39), give points at random, six to the left and two to the right. A curve, however, resembling a parabola may be drawn to include the points corresponding to the four alcohols, water, mercury (39),

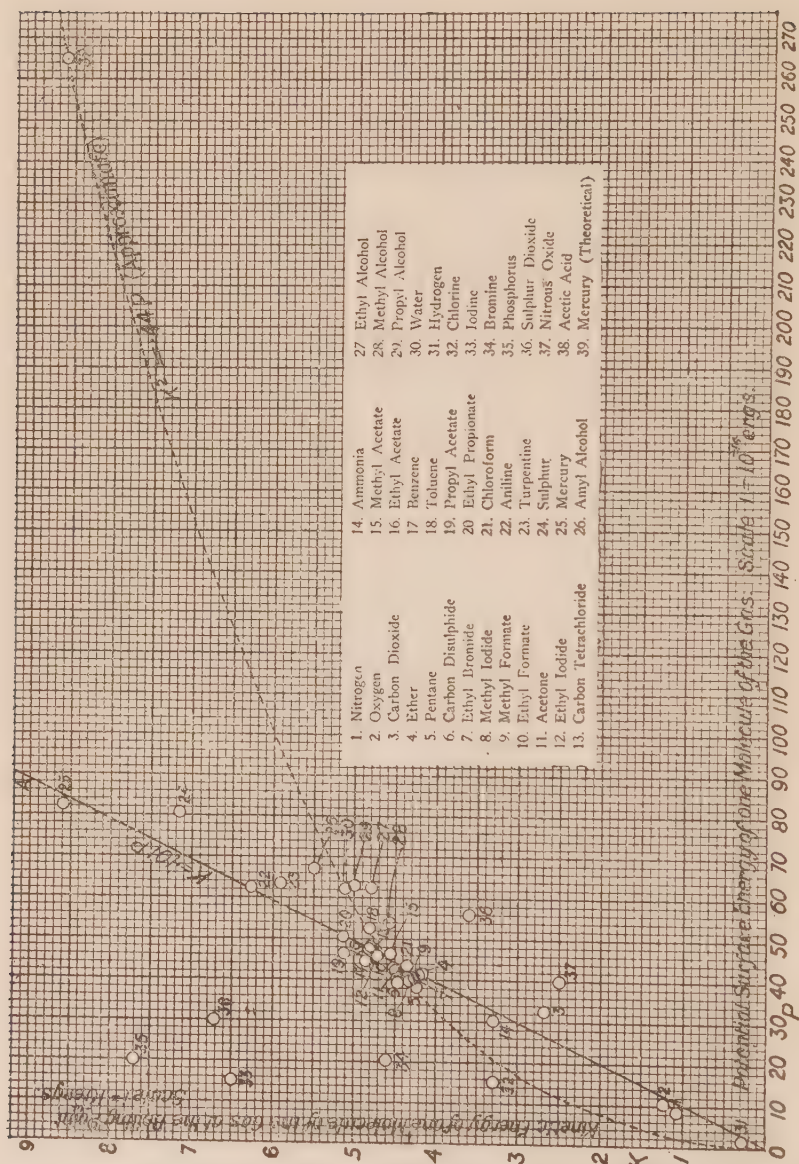


Fig. 5

hydrogen, and nearly all the others of the first twenty-five. The exceptions are sulphur, mercury (25), and, possibly, aniline and turpentine. For some reason acetic acid and nitrous oxide still seem to be excepted. An approximate equation to this curve is $y^2 = .44 x$. But, until more definite experimental knowledge is available in regard to the latent heats of these and other substances, it may not be advisable to attempt an exact statement of the law, even if such be possible.

Yet, whatever the statement of the law may be, it will be seen that the potential surface energy carried by each free molecule of the gas greatly exceeds its kinetic energy at the boiling point of the liquid. If Trouton's rule applies, it is ten times as much, while, if the parabolic relation holds, it is much greater than this for those substances whose boiling points are high. Moreover, the higher the boiling point the greater is the heat energy of the free molecule and, consequently, the greater is its potential surface energy. For instance, the heat energy of the gold molecule, which escapes from its liquid at a temperature of about 2800° A. , is 38.5×10^{-14} . But, if Trouton's rule holds good, its potential surface energy is 385×10^{-14} ; and, if the parabolic law applies, it will be as great as 3365×10^{-14} . In either case the evidence points to the conclusion that those substances that have high boiling points carry in their gaseous states a very great amount of potential surface energy about their free molecules. Now it so happens that the three elements, calcium, carbon, and silicon, which with their compounds are the chief constituents of the earth's crust, have extremely high boiling points. We may infer, then, on the evidence before us, that the total potential surface energy of these substances in their gaseous states was almost incalculably great; and, so long as the temperature was above their boiling points, this energy was latent and did not appear as heat.

If, therefore, we could conceive of a large mass of these gases separated in space from other gaseous masses and radiating its heat into space till its temperature was reduced to the boiling point of one or more of these substances,

coalescence would then take place. To the extent of this coalescence, the potential surface energy would be changed into heat, and this would raise the temperature automatically, and thus prevent further coalescence until the temperature should be reduced by radiation to the boiling point again. The process would be continuous, the free molecules coalescing at a rate depending on the rate at which heat is radiated into the surrounding space. Thus, there would be long periods (aeons) of time during which heat in enormous quantities would be radiated into space without the glowing mass becoming any colder. An analogous, though not precisely similar, case is that of steam condensing into water, where, instead of the heat produced by coalescence being carried away slowly by radiation, it is conducted away rapidly by the air and the sides of the containing vessel. In the former case, during the period of constant temperature, the gaseous mass would diminish and the liquid mass would increase until the whole had become liquid. This liquid mass would not necessarily form one body, but would consist of a number of masses of various sizes separated by wide spatial distances. Gradually, as these spherical masses grew larger, the curvature of the enveloping force and, hence, the internal pressure, would become less, so that the enclosed mass would gradually be freed from the control of its enveloping force. At the same time the force of gravity acting at shorter distances and with larger masses would at length become powerful enough, not only to hold the masses themselves together, but also to regulate the motions of the separate spherical masses among themselves.

After these gaseous substances had all condensed into liquid the glowing mass would cool down by radiation to the melting point and another period of constant temperature would begin. The potential energy, which in some unknown form exists in all liquids and which is known as the latent heat of fusion, would then begin to be converted into heat without change of temperature in the process of solidification. Thus there would be again a period of constant temperature while this heat was radiating into space, after which

the radiation would reduce the temperature indefinitely. We may conceive, in fact, the stars, nebulae, dark bodies, and gaseous space of the universe, as revealed by the modern telescope, to be but different stages in the evolution of the heavenly bodies through the operation of this law of coalescence in conjunction with the law of gravitation. The sun appears to be well advanced in the first period of constant temperature, while the planets and their satellites are long past the second stage for those substances that constitute the chief part of their mass. The earth is in the second stage for water, and has not reached the first radiating period for nitrogen and oxygen. The earth would soon reach the final stage of very low temperature were it not receiving from the sun an enormous and continuous supply of radiant energy which is quite, or more than, sufficient to make up the loss from its own radiation. The practical problem for man is to find out how to aid the natural processes by which the excess of energy from the sun is stored up as potential energy and so made available for his needs.

The nebular theory, which seeks to explain the solar system on the basis of the law of gravitation only, may, in the light of these conceptions, overcome many of the difficulties it has hitherto met with, and we may yet obtain a satisfactory account of the evolution of worlds and systems of worlds in ether space.

Finally, the peculiar difficulties that are inherent in the problem of determining by direct experiment the surface tension of solid bodies seem so far to be insurmountable. The preceding considerations, however, make it possible not only to fix an upper limit to this tension but even to determine an approximate value for it at any given temperature.

In column 4 of Table II (see page 59 for table) will be found the diameters of the space occupied by each of the molecules of the substances in the liquid or solid state as calculated from the formula

$$d = \left(\frac{6m}{\pi \rho_0 N} \right)^{\frac{1}{3}}$$

at the temperature at which ρ was determined. These diameters are somewhat greater than the actual mass diameters of the molecules. Knowing the value of P , the potential surface energy of the free molecule, we are able to find T_m , the tension of the enveloping force, from the relation $T_m = P/\pi d^2$. These will be found in column 7—we have assumed for reasons given in the previous article, that $T_m = T_o$, the tension about a large mass at 0° A. These are slightly less than the true values since the values of d are a little too great.

In column 5 we have recorded, as far as they are available from the standard tables, the surface tensions of large liquid masses of these substances as determined by actual experiment at the temperatures recorded in column 6. For sixteen of the thirty-eight substances these determinations are lacking. With one exception the measured tensions, as was pointed out previously should be the case, are less than the absolute tensions about the free molecules. The exception is mercury (25), for which there is reason to think that 59.7 for L should be 187 as given in (39). We may, then, reasonably conclude that for these sixteen substances the values of T in the last column form an upper limit to any future determinations of the surface tension of these substances as either liquids or solids. These limits are, of course, subject to any errors in the determinations for L and ρ_o .

Again, since T is known from the latent heat, if one determination for T is found, or the critical temperature of the liquid is known, at which T is zero, and if it be assumed that the temperature coefficient of surface tension is constant from 0° A. to θ° A., we may determine this temperature coefficient, and, therefore, also the surface tension at any temperature whether the substance is solid or liquid.

For instance, to determine the surface tension of ice at 161° A., which is the melting point of ethyl alcohol. Here for water $T_c = T_{638} = 0$, and $T_{288} = 74.4$, and, therefore, the change in tension for each degree is $74.4/361$, or 0.209 . Hence for water at maximum density $T_{277} = 75.7$. But during

TABLE II

No.	Name	$\rho\theta$	$d \times 10^8$	T_θ	θ°	$T_m = T_o$
1	Nitrogen.....	.810	4.78	8.5	78	11.3
2	Oxygen.....	1.14	4.46	13.1	90	15.75
3	Carbod Dioxide..	.772	5.64	30.1
4	Ether.....	.736	6.82	18.4	293	28.0
5	Pentane.....	.634	7.10	24.2
6	Car. Disulphide..	1.26	5.74	30.5	293	38.0
7	Ethyl Bromide...	1.45	6.19	33.0
8	Methyl Iodide...	2.28	5.82	39.6
9	Methyl Formate..	.986	5.77	39.8
10	Ethyl Formate...	.938	6.29	36.6
11	Acetone.....	.812	6.09	23.3	290	39.2
12	Ethyl Iodide....	1.944	6.33	36.5
13	C. Tetrachloride.	1.582	6.75	27.7	293	33.6
14	Ammonia.....	.623	4.41	48.9
15	Methyl Acetate..	.941	6.29	37.5
16	Ethyl Acetate...	.903	6.50	23.6	293	44.5
17	Benzene.....	.879	6.71	28.8	288	32.0
18	Toluene.....	.882	6.47	29.1	288	43.8
19	Propyl Acetate..	.891	6.08	18.9	283	49.3
20	Ethyl Propionate.	.896	7.11	31.9
21	Chloroform.....	1.26	6.68	29.3	293	31.1
22	Aniline.....	1.04	6.56	43	288	46.0
23	Turpentine.....	.865	7.92	38.5	294	32.3
24	Sulphur.....	2.00	3.70	42.1	384	167.5
25	Mercury.....	14.25	3.54	520	291	210
26	Amyl Alcohol...	.829	6.95	24.8	288	44.6
27	Ethyl Alcohol...	.806	5.65	22.2	288	61.9
28	Methyl Alcohol..	.812	4.99	24.7	288	69.6
29	Propyl Alcohol...	.817	6.10	25.9	279	54.0
30	Water.....	1.000	3.84	73.3	288	133.6
	Average.....					
31	Hydrogen.....	.07	2.25	8.8
32	Chlorine.....	1.507	4.21	23.6
33	Iodine.....	4.94	4.44	24.2
34	Bromine.....	1.74	5.26	23.7
35	Phosphorous....	2.20	3.55	50.8
36	Sulphur Dioxide.	1.434	5.21	66.0
37	Nitrous Oxide...	1.23	4.84	36.3	164	38.2
38	Acetic Acid.....	1.12	5.55	30.2	290	31.2
39	Mercury (Theor)	14.25	3.54	520	290	674

solidification the density decreases from 1 to 0.917, and, consequently, the surface of any spherical mass increases in the ratio of $(.917)^{\frac{2}{3}}$ to 1. Assuming that the total surface energy of the spherical mass is unchanged by the action of the internal forces of solidification, we have for ice at the melting point $T_{273} = 75.7 \times (0.917)^{\frac{2}{3}}$ or 71.5, and the change in tension for each degree in temperature is $(T_o - T_{273})/273$, that is, $(133.6 - 71.5)/273$, or 0.237. Hence the surface tension of ice at 161°A. is $133.6 - 161 \times 0.237$, or 95.4 dynes per centimetre.

The following is a brief summary:

(1) The kinetic energy of a free molecule at the boiling point and its potential surface energy are connected by a simple relation which is stated approximately by the equations $K = .101P$ or $K^2 = .44P$.

(2) The coalescence of free molecules and their separation again are effected through the operation of the same law, which is stated as follows: "Whenever two enveloping force areas come into contact, the areas in contact give up their potential surface energy, since the surface forces unite at the circumference of the common area and cease to act in that area."

(3) The energy, y , which is required to cause a molecule to emerge a distance of x above the surface of its liquid, is given by the parabolic law $y = T\pi x^2$; and the total P to cause complete dissociation, by the same law, is $P = T\pi d^2$.

(4) The relation in (1) above furnishes an explanation of the sun radiating its energy without lowering its temperature.

(5) The limit to the surface tension of solid bodies is given by the equation

$$T_o = mJL / N\pi d_o^2,$$

where

$$d_o = \left(\frac{6m}{\pi \rho_o N} \right)^{\frac{1}{3}}.$$

ARTICLE III

CAPILLARITY¹

In his excellent *Historical Notes upon Surface Energy and Forces of Short Range in Nature*, vol. 109, p. 375, 1922, W. B. Hardy remarks that "the exact way in which the attractive forces act in causing the rise of fluid in capillary tubes and the spreading of fluid over solid and fluid surfaces is still obscure." He evidently rejects all explanations by any Laplacean conception of molecular attraction. He probably holds that the explanation is to be sought in the modern electric theory of the constitution of matter, but that this theory has not as yet been developed far enough to throw sufficient light on the question. By the use of the term "attractive," however, he restricts the inquiry to a limited class of forces in terms of which these phenomena are to be explained. It is just possible that this restriction may preclude the solution of the problem.

That it is possible to conceive of a force which cannot be put in this class of "attractive" forces of short range may be shown. If a mass consisting of a single molecule exists at all, it has a position in ether-space at some particular instant. It may be considered isolated from all other masses. There is, therefore, a closed boundary within which there are properties differing from those not within this boundary. Any part of this closed boundary may be conceived as an area between space-regions called "mass" and "no-mass." If we say that *this enveloping area tends to become less*, we have defined a "force" which cannot be included in the class of attractive forces. Further, if we say that, *when two such enclosures come into contact, the tendency to decrease does not exist in the area of contact*, since there is no distinction of properties on opposite sides of this area, we have defined the law of the "force" for like masses. Finally, if we say that *when the two masses are unlike there is this distinction of properties and, consequently, a tendency of the common area to decrease*,

¹Reprinted from "*Nature*," September 16, 1922.

we have extended the law to unlike masses. Space will not permit the elaboration of these conceptions.

The question is: Does this "force" as conceived above really exist? Whether it does or not, repeated applications of the law as stated will account for surface tension of visible liquid and solid surfaces in terms of it. It will be admitted that the phenomenon of coalescence of visible spheres of like liquids is a direct application of the law. Also, in a letter on *Cohesion* in *Nature* (vol. 109, 1922),¹ the present writer has shown experimentally that visible exterior cohesion and adhesion in solids and liquids may be accounted for by surface tension forces alone, and, consequently, may be explained by molecular (surface) tension. Now these and even capillary rise and fluid spreading might conceivably be explained by intermolecular electric forces, though this has not yet been done; but it is difficult to see how the latent heat of a gas can be so accounted for, since in a gas the molecules are too widely separated to admit of short range intermolecular action at all, and the condensation of a gas, by which alone this great amount of heat is made available, is unattended by any chemical change or electrical effect. This latent heat, however, may be fully accounted for by molecular surface tension, as the writer has shown in the *Phil. Mag.*, vol. 41, p. 877².

Either, then, the latent heat of a gas must be otherwise accounted for, or the existence of molecular surface tension must be admitted. This in turn, it is true, may eventually be explained by the action of electric forces in the interior of the isolated molecule. In the meantime the writer offers the following explanation of capillary rise and surface spreading in terms of molecular tension as conceived above.

The following phenomena are illustrative: (a) If two free spheres of immiscible liquids be brought into contact, the mass of the one suddenly proceeds completely to envelop the mass of the other. (b) If a free liquid sphere and a small solid which does not dissolve in the liquid be brought into

¹Vide Article IV, p. 66.

²Vide Article I, p. 24.

contact, one of two actions takes place: either the mass of the liquid forms a closed sheath about the solid, or the mass of the solid *tends* to envelop the liquid, but is prevented by internal cohesion from assuming the necessary form. The liquid then stands out as a curved mound on the solid with a distinct "capillary" angle. With water, mercury acts as a solid metal. It is on this differential action of this surface force of water in union with the surface forces of small particles of minerals and rocks that the flotation processes for mineral separation depend.

When a liquid is in contact with a solid, there are three areas in which this *tendency to decrease* exists in different degrees, namely, the liquid-air, the solid-air, and the solid-liquid areas, the sum of the latter two areas being constant. At contact the only possible way in which these two latter tendencies can result in action is to decrease the solid-air area from its maximum by increasing the solid-liquid area from zero. Experiments show (*Nature, ibid.*)¹ that this change always proceeds to some extent. In the case of water and rock it proceeds until *all* the solid-air area becomes solid-liquid area. It does not reach this limit in the case of water and a mineral.

But the extent of this fluid-spreading depends further on (1) the tendency to decrease of the liquid-air area, unrestricted by internal cohesion, (2) the force of gravity acting on the liquid mass, (3) the form of the solid area, and (4) the amount of the liquid. Thus, a small drop of an oil such as oleic acid may not spread far on a horizontal glass surface, since the decrease in the glass-air area involves increases in both glass-oil and oil-air areas; whereas in capillary rise this decrease does not involve any increase in oil-air area. The oil will, therefore, ascend until its increasing weight balances the tendency to decrease (tension) in the glass-air area within the tube. Again, a hanging drop of the oil will completely envelop a large fragment of glass and hold it against its weight.

It is plain, then, that methods of measuring surface tensions of liquid-air and liquid-liquid areas should be, as

¹Vide Article IV, p. 66.

far as possible, free from errors arising from unknown changes in liquid-air areas and from the unknown solid-air and solid-liquid tensions. It will be seen that the capillary rise method in reality does this, although there is difficulty in measuring the internal bore and keeping it clean. But the following arrangement seems to be as nearly as possible free from these objections, and to be adapted to measure the tensions of interfacial liquid surfaces as well.

The liquid (mercury excepted) is made to drop from a fine capillary tube having thin walls as in Fig. 1. In forming the drop, it spreads upward over the exterior surface and reaches a limiting size, shape, and position. It then slips down the tube at a uniform velocity with little modification in size or

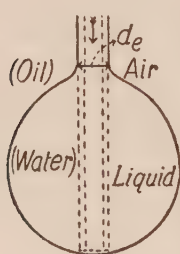


Fig. 1

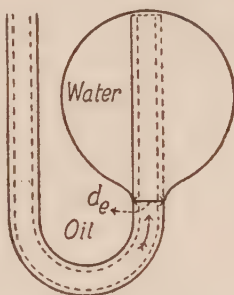


Fig. 2

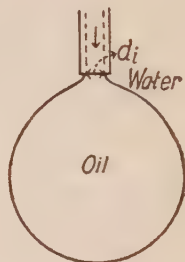


Fig. 3

shape, and after suffering a slight check in its motion breaks its connection and falls. We may then equate the whole tension about the tube with the weight of the drop, so that

$$T_{la} \times \pi d_e = W_L$$

or

$$T_{la} = W_L / \pi d_e,$$

where T_{la} is the liquid-air tension and d_e is the external diameter of the tube.

The same drop formation occurs when the tube is arranged to drop water downwards into any lighter oil, or by a bent tube (Fig. 2) upwards into a heavier oil. In this case we have the

equation

$$T_{wo} = \frac{W_w}{\pi d_e} \times \frac{\rho_w - \rho_o}{\rho_w},$$

where the suffixes w , o , e and i denote the words water, oil, external, and internal, and ρ is density, from which the tension of the water-oil surface may be calculated.

On the contrary, when oil is dropped either downwards or upwards into water, it does not spread on any exterior water-glass surface, but forms its attachment as in Fig. 3. In this case we have

$$T_{wo} = \frac{W_o}{\pi d_i} \times \frac{\rho_w \sim \rho_o}{\rho_o}.$$

These all give results agreeing with those recorded in the standard tables.

In accordance, then, with this conception of an elemental force not included in the class of "attractive" forces, we should expect that these changes in area would always be attended by a rise in temperature. If it be asked why the enveloping area about a free molecular mass tends to decrease, there is no answer; and neither is there an answer to the question as to why any mass tends to approach another mass.

ARTICLE IV

COHESION AND ADHESION*

In a recent article on *Cohesion* published in *Nature*, August 18, 1921, Dr. Herbert Chatley, after reviewing the various theories put forth as to the nature of the force by which the particles of a substance cohere, and after referring to the different phenomena occurring in connection with its action, says: "It is difficult to conceive of one force having all these properties, but perfectly simple to imagine an attraction and repulsion combined that will do so, *provided that the attraction decreases more slowly with separation than the repulsion.*" Now the theories referred to, along with Dr. Chatley's new one, are all based on centrally directed forces, either gravitational, or electrical; but, while rejecting Sutherland's statement that cohesion is independent of gravitation, he does not claim to have solved the problem of the relation between them—a problem of "the highest practical importance".

Now, both gravitational and electrical attraction and repulsion obey the inverse square law, and the difficulty of explaining cohesion in terms of either, or both, of these forces seems to be that the force of cohesion is almost inconceivably greater than the force of gravitation, and that the law of the electrical forces ceases to operate the instant that the two bodies come into contact. It is doubtful, then, that the force of cohesion can be a linear function of these two known fundamental forces, an opinion which Dr. Chatley seems to hold when he states his belief that the force of cohesion is not, on the principle of unity, independent of the forces obeying the inverse square law. If cohesion involves the distance in other powers than -2 , it is difficult not to agree with Sutherland who says that they have nothing to do with each other.

It is a matter of universal observation that two free liquid drops immediately coalesce when they are brought into

*A shorter account of the phenomena dealt with in this paper appeared in *Nature*, under the title *Cohesion*, Vol. 109, p. 413, 1922.

contact. The force which causes this coalescence appears to be more of the nature of a force *enveloping* their masses than of a force *attracting* their masses. It is known as surface tension, and was observed by Maxwell and others to have enveloping properties. It is commonly explained by molecular attraction, an hypothesis which is due to Laplace.

But the writer has adduced in the *Philosophical Magazine*¹ (41, 877, 1921), very strong, if not conclusive, evidence that the same force also acts about free molecular masses, and cannot, therefore, be due to molecular attraction. The alternative is that it is *an elemental force acting not in lines but over areas*. This force can fulfil the conditions imposed in an explanation of cohesion and adhesion.

The conception that surface tension is a force enveloping mass down to molecular dimensions appears to have been rendered almost impossible by the theory of surface tension which made it depend on molecular attraction. But besides this, there is a natural reason why this two-dimensional force, if such it be, has not been recognized before. Through the impetus given to the study of geometry by the Newtonian analysis great additions have been made to our knowledge of straight and curved lines or of one-dimensional space. Again, mass, volume, and even weight, which are conceptions of three-dimensional space, readily lend themselves to measurement by physical means regardless of their geometrical form. But, except for planes and a few geometrical solids, there is no device either geometrical or physical for measuring the surface of bodies. This inability to think in two-dimensional space, which results from lack of knowledge of surface, becomes evident when we reflect that we always estimate the size of an object, such as a ball, in terms of its diameter or of its volume, never in terms of its enveloping surface. Yet, from a scientific point of view, two-dimensional space is as important as space in one or three dimensions; and, while we sometimes associate volume and diameter with a molecular mass, we rarely think of a molecular mass as possessing

¹Vide Article I, p. 24.

any surface properties. Much less do the present theories of atomic structure admit of the two-dimensional surface concept.

Now it would be in accord with the principle of unity, to which Dr. Chatley alludes, to conceive of the forces of nature as corresponding to these three geometrical concepts of space. Centrally directed forces such as gravitation would correspond to the one-dimensional space; surface tension in its enlarged meaning suggested above would correspond to the two-dimensional space; while pressure, such as that force located in mass which conserves the volume of that mass, would correspond to the three-dimensional space. Thus, in a system of masses controlled by centrally directed forces, a change of potential energy would result from a change in the distance between the masses; in a system controlled by surface tension forces, a change in potential energy would result from a change in the enveloping area; while in a system of mass controlled by pressure a change in potential energy would result from a change in the volume occupied by the mass.

The question now arises:—Is cohesion explainable in terms of this enveloping surface force instead of in terms of the centrally directed forces referred to by Dr. Chatley. If we conceive of two free molecules behaving towards each other as liquid spheres are observed to do down to the smallest microscopic sizes, we shall at least be able to regard the problem from a new point of view. But, fortunately, there is very definite and easily verifiable evidence that cohesion, as well as adhesion, is due to a surface force, whatever be its nature, as may be seen from the following simple experiment which will be published in fuller detail later.

It was found that a small sphere of mercury¹ resting on a sheet of paper could be lifted up against its weight by bringing a hanging water drop to touch it from above. Accordingly spheres of mercury were attached to the water, ranging in size from .085 mm. to 1.54 mm. in diameter, and from .0043 mg. to 25.5 mg. in weight. In no instance was the mercury sphere wholly covered with the water, but it fitted,

¹Vide Article V, p. 74, et seq. for illustrations bearing on these experiments.

as it were, into an inverted hemispherical cavity in the water. From measurements made on these it was found that the upward vertical force exerted by the surface tension of the water in the periphery of the contact area was *always more than sufficient* to support the weight of the mercury. For the smallest sphere the vertical force was as much as seven times the weight. As the suspended spheres became larger, this ratio decreased by a hyperbolic law until, for the largest spheres that could be held without falling off, the vertical force became very approximately equal to the weight.

Similarly, mercury spheres were suspended from horizontal glass and mica surfaces and measurements made as before. These spheres ranged from .046 mm. to 2.25 mm. in diameter, and from .0007 mg. to 78 mg. in weight. Here the vertical force exerted by the surface tension of the mercury (liquid) in the periphery of the contact area greatly exceeded the weight supported. For the smallest sphere (of microscopic size) it was 6,800 times the weight; and, as before, this ratio decreased by a hyperbolic law to 1.93 for the largest sphere that could be supported. But if the surface tension of glass having a theoretical value of about 285 dynes per cm. had been used in the calculations instead of that of mercury which was taken as 547 dynes per cm., the ratio would have decreased by a hyperbolic law from 3,550 to a ratio of equality as before. In either of these experiments had the vertical force been *less than the weight supported*, it might be concluded that there was a force attracting the molecules, which were on opposite sides of the common area, to one another. *But such was not the case.*

In the first experiment, when the water which formed the connecting link between the mercury sphere and the surface above was allowed to evaporate, the mercury sphere was gradually lifted up and became attached to the glass or mica surface, thus transferring the strain from the surface tension of the water to that of the glass or mica. But no substantial difference in the measurements could be found from those where the mercury was attached directly to the surface as in the second experiment.

In the same way small mercury spheres as great as 1.5 mm. in diameter floated with great persistence *above* a clean water surface. As before the mercury fitted into a hemispherical cup and its weight was supported by the vertical component of the surface tension of the water in the periphery of the contact area, the upper portion of the sphere being free in the air. From the fact that the weight of the mercury caused a wide circular depression in the water surface and that the upper rim of the mercury sphere was above the general level of the water, it may be inferred that the vertical force was capable of supporting more than this weight if the sphere was pressed down so that its upper rim was even with or below the level of the water.

Further, comparatively large particles of glass, rock, metals, and other solids were in this manner lifted up against their weights on the lowest rim of a water drop, and by the evaporation of the water became firmly attached to any smooth surface above. Experiment also showed that two glass spheres, two centimetres in diameter, when held together by a neck of water alone still remained attached after the water evaporated; and that the force then required to separate them was *three times as great* as that required to do so against the pull of the water neck. Also small particles of freshly powdered glass attached themselves by direct contact to the face of a diamond so firmly that they were not dislodged even when jarred by a sharp blow.

The evidence of these experiments goes to show that, in all cases where measurements could be made, *the forces of cohesion and adhesion are simply surface tension forces pulling in the periphery of the contact area perpendicularly to that area.* It also goes to show that, as the particles decrease in size down to microscopic dimensions, these forces in comparison with the mass (or weight) become greatly increased. Now, there is no reason to think that the same law cannot operate when the particles become so small as to be invisible down to molecular dimensions. In fact the writer has found almost conclusive evidence from another source (Phil. Mag., Vol. 41,

p. 884, 1921) that the law does hold for two free molecules of a gas.

On the other hand, the experiments furnish no evidence whatever that cohesion and adhesion are due to centrally-directed forces, gravitational, electrical, magnetic, or any other. Dr. Chatley states that the force of cohesion is of the order of 10^{-6} dynes. By calculation the binding force of the surface tension holding two water molecules together in a sphere is 2.05×10^{-5} dynes; and the central force of repulsion between two molecules of the same size each carrying a charge of one electron has a maximum value of 6.2×10^{-5} dynes. For mercury these forces are 7.69×10^{-5} dynes and 4.49×10^{-5} dynes respectively.

Further, the range of action of this enveloping surface force, in the case of two molecules about to cohere (coalesce), has a maximum value of two molecular diameters. This corresponds to, and explains, what is commonly referred to as the range of molecular attraction, which was first postulated by Laplace and over which so much controversy has arisen. Again, the compression upon a double molecular mass of water, induced by the spherical curvature in which this enveloping force acts, is, by Laplace's law, $P = 4T/d$, equal to $4 \times 133.6 / (\sqrt[3]{2} \times 3.85 \times 10^{-8})$ dynes, or 12,000 atmospheres—a pressure which is quite sufficient to hold the two molecules together and which is known as the intrinsic pressure of water. Thus it appears possible that there is a single force which will account for all the properties of cohesion and of adhesion as well.

This conception of the cause of molecular action appears, then, to be in reality fundamental. In itself it solves the problem of surface tension. It accounts satisfactorily for the disappearance of the energy known as the latent heat of condensation (*Phil. Mag., ibid.*). It explains, as we have seen, both cohesion and adhesion. But besides all this there is the remarkable coincidence that this enveloping surface force is located, or performs its function, in the precise area bounding free mass in which the phenomena of reflection and

refraction of light takes place and electrons have their movements. These considerations give point to Dr. Chatley's concluding statement that "It is conceivable that . . . the complete solution of the microscopic properties of matter would also solve the question of the inner structure of molecules and atoms".

SYNOPSIS

The nature of surface tension. From evidence presented in the *Philosophical Magazine*, Vol. 41, pp. 877-889, 1921, on *The Coalescence of Liquid Spheres—Molecular Diameters*, it is inferred that the force of surface tension is a fundamental property of all free surfaces of mass, acting about the free molecular masses of a gas and causing the molecules to coalesce or cohere in the same way as liquid spheres are observed to do.

Adhesion between mercury and water. Accordingly, measurements were made on mercury spheres suspended from the lowest rims of water drops. These ranged in diameter from .06 mm. to 1.5 mm. The vertical lift upon the mercury of the surface tension of the water was compared with the weight of the suspended sphere and it was found that the vertical lift was always greater than the weight supported except when the spheres, on account of their size, were on the point of falling off and then these two forces tended to become equal. For the smallest sphere the vertical lift was about seven times the weight.

Adhesion between mercury and glass. Similar measurements were made on mercury spheres suspended from glass surfaces. These ranged in diameter from .02 mm. to 2.25 mm.; and, as before, the vertical lift of the surface tension of the mercury at the line of its attachment to the glass was compared with the weight of the suspended sphere. It was found that, as the spheres increased in size, the vertical lift gradually decreased from about 13,000 to 2.29 times the weight. Had the surface tension of glass having a value of 339 dynes per cm. been used instead of that of mercury, this

ratio would have decreased from 6,000 for small spheres to one of equality as the spheres were on the point of falling off.

Solid surfaces. Similar measurements in the case of small solid bodies suspended from water and of bodies adhering to each other with or without a liquid connecting link showed that, as far as could be observed microscopically, the same law was in operation.

The law of cohesion extends to molecular dimensions. Also from the evidence referred to above there is reason to think that the law operates as well in the case of molecular masses, that is:—*Cohesion and adhesion are simply surface tension forces, which exist about all free masses molecular or larger, attaching themselves to each other in the periphery of the contact area and binding the two masses together in one enveloping surface tension force.*

There is no evidence of any molecular attraction between the two masses in the contact area itself, but an actual pressure of the one mass upon the other reaching in the case of the water molecule to about 13,000 atmospheres.

ARTICLE V

EXTERIOR COHESION AND ADHESION OF LIQUIDS AND SOLIDS

Introduction.—Cohesion or molecular attraction has been generally held to obey the law

$$F = kd^{-x},$$

where k is some constant, x some number greater than 2, and d the effective range of the force. Experimental evidence, however, has not revealed any definite value for x , and there is some doubt that the law is of this form.

The importance of the question led the writer to attempt to measure this force in order, if possible, to identify it with that which causes the coalescence of liquid spheres, an account of which was published in the *Philosophical Magazine*, Vol. 41, pp. 877-889, 1921.¹

Adhesion between Mercury and Water.—It was found that small mercury spheres could be lifted from a sheet

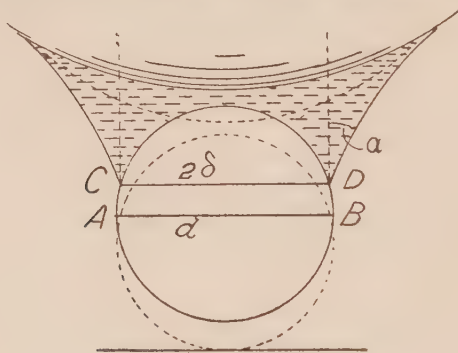


Figure 1.

of paper and hung suspended against their weights by bringing water drops to touch them from above, as shown in Fig. 1. Spheres up to a diameter of 1.5 mm. were thus supported. Examination showed that the water surface appeared attached to the mercury sphere about a horizontal circle CD , diameter 2δ , thus forming a well-defined angle with the mercury surface in any central vertical plane. This circle was

¹Vide Article I, p. 24.

TABLE I—*Mercury suspended from water.*

No.	$d \times 650$	$2\delta \times 650$	α	W in dynes	T in dynes	T/W
1*	4	3.6	89 30	0.00159	0.0111	6.99
2	6	5	89 12	0.00551	0.0243	4.50
3	7	7	89	0.00875	0.0635	7.22
4	8	8	88 30	0.0131	0.0742	5.70
5	9	9	87 24	0.0186	0.100	5.39
6	10	10	88 06	0.0254	0.118	4.63
7	11	11	87 42	0.0339	0.156	4.61
8	13	13	87	0.0560	0.240	3.28
9	15	15	86	0.086	0.370	3.30
10	17	17	86 12	0.125	0.471	3.19
11	20	20	84 54	0.204	0.651	3.09
12	22	22	84 36	0.271	0.734	2.71
13	25	25	83 30	0.398	1.00	2.52
14	27	27	81 15	0.502	1.47	2.95
15	27	25	83 18	0.502	1.04	2.06
16	30	30	81 12	0.759	1.68	2.22
17	34	34	79 30	1.00	2.20	2.20
18	37.5	37.5	78	1.34	2.75	2.05
19	40	40	76	1.63	3.43	2.10
20	45	43	72 54	2.33	4.48	1.93
21	50	49	74	3.19	4.90	1.50
22	55	55	71	4.25	5.93	1.40
23	60	57	65	5.50	8.51	1.55
24	70	49	49	8.22	12.5	1.49
25	79	76	43	12.56	19.4	1.55
25 z	79	59	53	12.56	12.5	1.00
26	85	65	22	15.64	21.3	1.36
27	92	88	33	19.9	26.1	1.31
28	94	35	35	21.3	22.6	1.06
29	95	95	28	21.8	29.8	1.37
30	99	95	31 30	24.7	28.7	1.16
31	105	(95)	(28)	29.5	(29.8)	(1.01)

*See Fig. 2 for smallest sphere.

zNo. 25 just before it fell off.

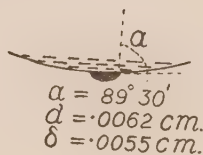


Figure 2.

approximately equatorial, being only slightly above the equator, AB , for large spheres and below it for small ones.

The upward vertical component T , of the surface tension σ , of the water was then calculated from the formula

$$T = \sigma \cdot 2\pi\delta \cdot \cos \alpha \quad (1)$$

where $\sigma = 73.3$ and α is the inclination of the water surface from the vertical. The weight W was calculated from the diameter by the usual rule. A few of the results obtained are given in Table I, the others only confirming these. Considerable difficulty was experienced in measuring the very small spheres on account of the vibrations of the hanging drop and the very large ones on account of their tendency to fall off when near the limit of their size.

Ratio $\frac{T}{W}$

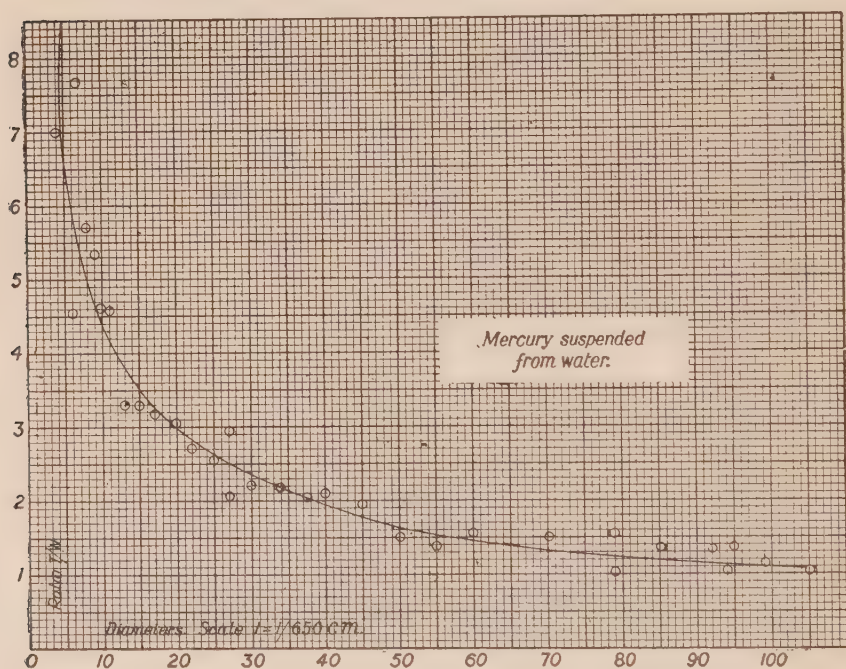


Figure 3.

Diameter

The results show (a) that the vertical component of the surface tension of the water at the line of its attachment to the mercury is always greater than the weight supported and, therefore, is sufficient alone to account for the adhesion of the mercury to the water: (b) that T tends to become equal to W when the spheres are about to fall off; and (c) that there is an actual pressure of the water molecules upon the mercury molecules in the contact area itself. This pressure is evidently accounted for by Laplace's formula,

$$T - W = \pi \delta^2 \left(\frac{\sigma}{r_1} + \frac{\sigma}{r_2} + hg \right) \dots (2)$$

where r_1 and r_2 are the principal radii of curvature of the water surface and h is the height of the water. In Fig. 3 d has been plotted against T/W .

Adhesion between Mercury and Glass.—Again, when the water, Fig. 1, was allowed to evaporate, the mercury was lifted up and became attached to the glass, as in Fig. 4. In many other ways also mercury spheres were attached to glass surfaces, reaching a diameter in one instance of 2.25 mm. As before, the upward vertical component of the surface tension of the mercury along the line of its attachment to the glass was calculated by formula (1) and compared with the weight of the mercury. The results are given in Table II.

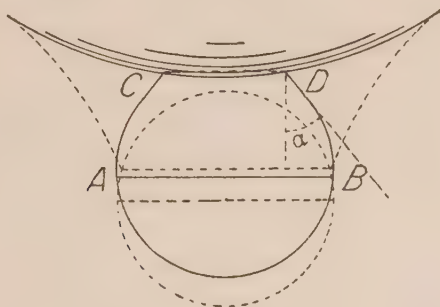


Figure 4.

In this case the magnitude of the ratio reached the extraordinary value of about 13,000 in the case of the smallest

TABLE II—*Mercury suspended from glass.*

No.	$d \times 650$	$2\delta \times 650$	α	W in dynes	T in dynes	T/W
			°			
1	1.7	1	50	0.000125	1.70	13,600
2	2	1.3	50	0.000204	2.21	10,800
3	3	2	38	0.00069	4.17	6,060
4	3.5	2.3	38	0.00110	4.80	4,360
5	4.2	3	36	0.00188	6.42	3,440
6	4.7	3	37	0.00265	6.34	2,390
7	6	4	37	0.00507	8.45	1,670
8	6	3	45	0.00507	4.45	805
9	8.5	5	45	0.0156	9.34	598
10	9.5	5.5	43	0.0218	10.89	499
11	12	6	50	0.0438	10.2	233
12	13	6.5	47 30	0.0560	11.6	207
13	14	8	47 30	0.0700	14.3	204
14	15.4	8.6	47 30	0.0930	15.4	165
15	19	10	47 30	0.175	17.9	102
16	22.5	12.5	47 18	0.290	22.4	77
17	25	14	47 24	0.398	25.1	63
18	28.5	15.4	47 30	0.590	27.5	47
19	42.5	24	48	1.94	42.5	22
20	45	25	46	2.33	46.0	20
21	51.5	32.5	48 24	3.32	57.1	16.8
22	56.5	41	49	4.49	71.0	15.8
23	66	34	47 30	7.32	60.8	8.3
24	72	39	47 30	9.51	69.7	7.34
25	78.5	28	57	12.3	50.8	4.12
26	80	35	51	13.05	58.3	4.47
27	94	56.5	40	21.2	114.6	5.42
28	104	54.5	43	27.1	105	3.89
29	111	70	37	34.8	148	4.25
30	117	67	37	40.8	142	3.47
31	135	55	34	49.8	121	2.49
32	127	70	34	52.2	154	2.94
33	130	73	31	56.0	159	2.85
34	135	73	30	62.7	161	2.56
35	138	75	30	67.0	166	2.47
36	140	75	30	69.9	166	2.37
37	146	73	29	79.3	163	2.05
38	148	70	27	82.6	159	1.93

sphere, and decreased regularly as the spheres became larger to a value of about 2.29 (the average of the last five) for those at the point of falling off. However, had 239 been used for σ in the calculations instead of 547, the value of σ for mercury, the ratio would have decreased from about 6,000 to one of equality, as might have been expected from the previous case. It may be assumed, then, that the glass would have a surface tension approximately equal to 239 dynes per cm.

As before, these results show (a) that the surface tension of the glass (or mercury) is sufficient alone to account for the adhesion of the mercury to the glass against its weight; (b) that in the contact area itself there is an actual pressure of the molecules of the glass on the molecules of the mercury sufficiently great to cause a large plane area to be impressed on the upper side of the mercury sphere. This pressure is accounted for by the formula

$$T - W = \pi \delta^2 \left(\frac{\sigma}{r_1} + \frac{\sigma}{r_2} \right) \dots (3)$$

where r_1 and r_2 are the principal radii of curvature of the mercury near the line of its attachment to the glass.

In Fig. 5, T/W has been plotted against d for the larger spheres where $\sigma = 239$. The curve has a definite equation of the form

$$x^2 y = \frac{6\sigma}{\rho g} \cos^2 a \dots (4)$$

which holds true until the spheres, on account of their weight, cause the angle a to become less than $47^\circ 30'$.

Again, mercury spheres were found to float on the surface of water contained in a vessel, as in Fig. 6. They reached a limit of nearly 1.5 mm. in diameter, and were evidently supported chiefly by the surface tension of the water pulling with an upward component at the line of contact CD , though actual measurements were impossible. In both Fig. 1 and Fig. 6 the downward curvatures of the water surface are caused by the gravitation of the earth. In a region of space where such gravitation of a third body would be small it may be

Ratio
 $\frac{f}{W}$

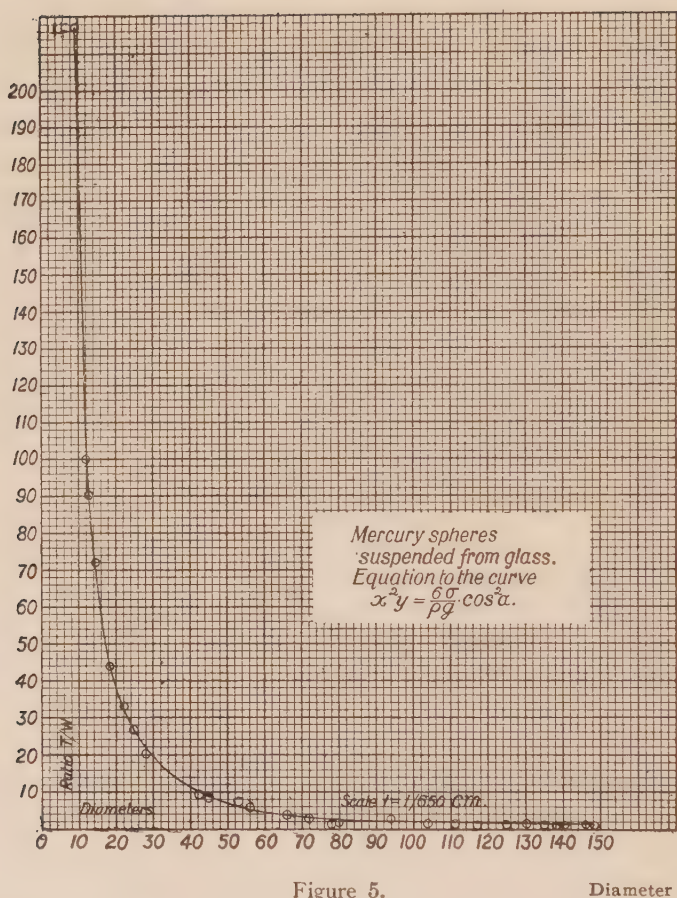


Figure 5.

Diameter

inferred that a mercury sphere in contact with a large water mass would cause no curvature in the water surface and the attachment would be as shown in Fig. 7.

Fig. 8 shows mercury spheres as they appear attached underneath a plane glass surface. Until they suffer deformation on account of their weight, the angle α is very

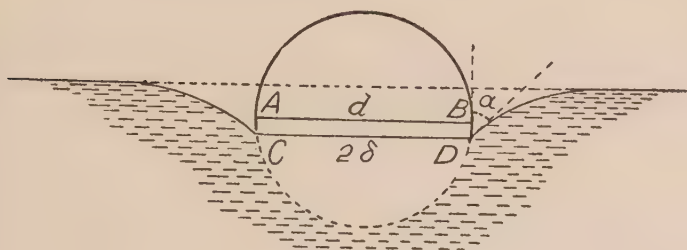


Figure 6.

approximately constant and equal to $47^{\circ} 30'$. Provided all the surfaces are clean, the form the spheres assume is independent of the method by which they were attached, whether by

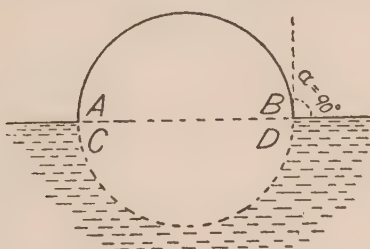


Figure 7.

direct contact, by indirect contact by means of evaporating water, or by condensation of mercury vapour.

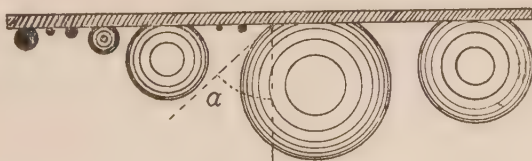


Figure 8.

Adhesion of Solids to Liquids.—Instead of mercury spheres small metal discs were hung suspended from water

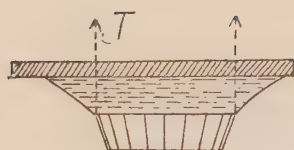


Figure 9.

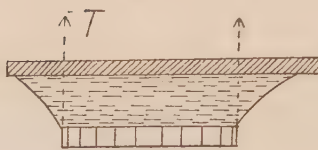


Figure 10.



Figure 11.

as in Figs. 9, 10 and 11, and measurements for T and W were made as before. In Fig. 11, T was found to be less than W , and the disc could not be supported unless the water was less than 1 mm. thick. Then the curvature in a central vertical plane was great enough to induce a negative pressure, or stretching effect, on the volume of the water, which with T was sufficiently great to support the disc as shown in the figure. The result is given in Table III.

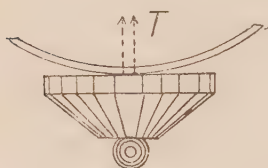


Figure 12.

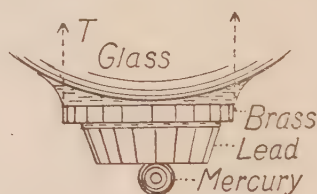


Figure 13.

The whole force of the attachment may then be represented by a modified form of formula (3),

$$F = 2\pi\delta\sigma\cos\alpha + \pi\delta^2\left(\frac{\sigma}{t} - \frac{\sigma}{\delta}\right) + F_m \dots (5)$$

where t is the radius of curvature at the edge, 2δ the diameter of the water lamina, and F_m a small force due to the contact

TABLE III
Solids Supported by Water Film.

	2δ	W	T	T/W
Fig. 7, lead frustrum...	.23 cm.	46 dynes	52 dynes	1.13
Fig. 8, brass disc.....	.50 "	81 "	112 "	1.36
Fig. 9, brass disc.....	.48 "	181 "	133 "	1.33
Force due to curvature.....			133 "	

of the solid surfaces and of solid particles in the water mass itself.

Indirect Adhesion of Solid Surfaces.—Now, as in the case of mercury, it was found that, when the water had apparently all evaporated, the solid surfaces still remained attached with a much stronger force. A microscopic examination of the diminishing water circle showed (*a*) that the water retained a clear outline until its diameter became less than a mm., (*b*) that a regular disintegration of the water film then took place, (*c*) that some solid particles appeared wedged in between the two surfaces, even outside the disintegrating mass, and (*d*) that traces of smaller solids seemed to be irregularly distributed over the disintegrated area. The strong attachment of the two solid surfaces thus appeared to be due, first to the direct contact of the molecules in the surfaces themselves, and secondly to the double contact of the solid particles between the surfaces.

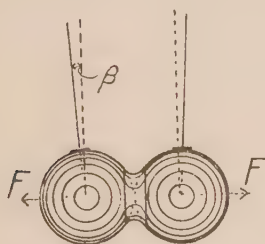


Figure 14.

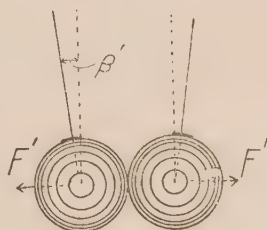


Figure 15.

In order to measure the magnitude of this (dry) attachment, spheres of glass and of brass were suspended by silk threads from supports whose distance apart was adjustable. In Fig. 14 the force required to break the water connection between the spheres was calculated from the angle, β , of inclination of the thread from the vertical. When the water had evaporated, Fig. 15, a similar calculation was made from the angle β' . The results are given in Table IV. They show that the adhesion is about three times as great after the evaporation of the water as it was before.

TABLE IV

Glass sphere (a), weight 4356 dynes, length of thread 93.3 cm.					
β ° ,	β' ° ,	F	F'	F'/F	
2 37	5 34	199 dynes	423 dynes	2.12	
2 36	5 05	156 "	385 "	2.47	
2 37	6 26	158 "	488 "	3.09	
2 23	6 08	180 "	465 "	2.58	
2 18	7 19	174 "	555 "	3.19	
Average	2 30	173 "	463 "	2.69	
Glass sphere (b), weight 6615 dynes, length of thread 68 cm.					
β ° ,	β' ° ,	F	F'	F'/F	
1 45	2 33	197 dynes	296 dynes	1.50	
1 40	5 15	191 "	603 "	3.15	
1 48	6 14	207 "	718 "	3.46	
1 48	5 34	207 "	642 "	3.09	
Average	1 45	200 "	564 "	2.69	
Brass sphere (c), weight 8686 dynes, length of thread 72.5 cm.					
β ° ,	β' ° ,	F	F'	F'/F	
0 54	2 54	127 dynes	440 dynes	3.22	
0 53	2 59	134 "	452 "	3.29	
0 53	2 33	134 "	387 "	2.90	
Average	0 53	135 "	427 "	3.14	

The Second Term of Equation (5).—Until the contracting water lamina between the two spheres begins to disintegrate the following theoretical investigation applies:—

Let d be the diameter of the spheres, 2δ the width of the water lamina, and $2t$ its thickness at the outer edge, at which it may be assumed that $r_1=t$ and $r_2=\delta$. It then follows by elementary geometry that

$$t(t+d)=\delta^2.$$

Since t is small in comparison with d , we have approximately

$$t=\delta^2/d.$$

This enables the second term on the right of formula (5) to be written

$$P = \pi d \sigma \quad . \quad . \quad . \quad . \quad (6)$$

which shows that it denotes a force proportional to the diameter of the spheres but independent of the width of the water lamina.

In Fig. 15, where $d = 1.5$ cm., this term gives 341 dynes which agrees very well with the measured force as shown in Table IV.

Again, the magnitude of the second term in formula (5) may be seen in the case of two plane surfaces as follows: A shallow vessel of thin glass with its upper edge polished smooth and level, when filled with water may be fitted under a thick piece of plate glass by pressing the vessel against the glass and carefully absorbing all the extra water about the top with blotting paper. The force of the attachment is found to be very great. When the water between the edge of the vessel and the plate shows interference colour bands, its thickness is of the order of the wave length of light. If $2t = .00014$ cm. and the diameter of the vessel be 10 cm., this second term gives a total force of about 84 kg. in weight and causes a stretching stress on the water equivalent to a pressure of one atmosphere.

In one case, after such an attachment lasting for more than two months against a weight of 2.26 kg., the stretching stress became so great as to cause the bottom of the vessel to collapse without fracturing the sides. This was due to the increase in the curvature of the water lamina made thinner by the evaporation of the water at the outer edge.

But it is doubtful whether under ordinary atmospheric conditions the water between two solid surfaces, or between two solid particles of any kind, ever does completely disappear by evaporation, and consequently, much of the adhesion commonly observed is of the type described above. It is further illustrated on a large scale in Fig. 16, where glass rods are supported against their weight by means of mercury spheres; in Fig. 17, where mica plates are attached to glass and to each other by the same means; and in Fig. 18,

where a glass rod fractured at *C* is held together by a thin lamina of water when supported at the ends by threads.

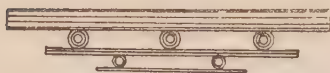


Figure 16.

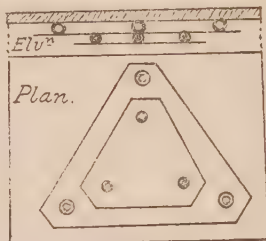


Figure 17.

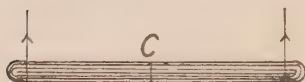


Figure 18.

Direct Cohesion of Solids.—There is, however, abundant and conclusive experimental evidence that small, clean, freshly-broken solid particles do adhere by direct contact to freshly-cloven solid surfaces of all kinds, with forces which, though they are too small to be measured, are able to resist very powerful jarring efforts to detach them. The gripping effect which two clean, smooth metal surfaces have for each other when brought into contact indicates that a comparatively large number of surface molecules have come into contact and coalesced in the same way as a small mercury sphere attaches itself to glass, that is, by the action of surface tension forces.

The Law of Cohesion and Adhesion.—Now there has been adduced from another source altogether¹ very strong evidence, if not complete proof, that the surface tension force which causes visible liquid spheres to coalesce, or cohere, also causes free molecules to do so; and, since on the experimental evidence presented above, this force accounts for the cohesion and adhesion of visible liquid and solid masses, it is reasonable to conclude that it acts in the same way in the

¹Vide Article 1, p. 24.

case of invisible masses down to the free molecules themselves. Assuming this conclusion to be true—and the writer has not been able to find any experimental evidence pointing to an alternate view—the law of cohesion and adhesion as applied to masses down to molecular dimensions may be stated as follows:—

Cohesion and adhesion are due to surface tension forces which, existing about all free masses of molecular or larger dimensions, unite on contact with each other in the periphery of the common area, and thus bind the two masses together through one enveloping surface tension force.

Comparison of Cohesion with other Forces.—In order that this force may be compared with other known forces the magnitudes of various molecular forces have been calculated in dynes. These are given in Table V, where we take

$$F_s = \pi 2^{\frac{1}{2}} d \cdot \sigma$$

the coalescing force holding two molecular masses in one sphere;

$$F_e = e^2 / (2d)^2$$

the electrical repulsion between two ionized molecules nearly in contact;

$$F_g = G \left(\frac{m}{N} \right)^2 / d^2$$

the gravitational attraction of two molecules nearly in contact; and

$$P_m = 4\sigma / d$$

the molecular pressure in dynes per sq. cm. on the mass due to the tension force in the spherical surface of the molecule. The data for d and σ are taken from the article referred to¹.

TABLE V

	d	σ	F_s	F_e	F_g	P_m
Mercury	3.56×10^{-8}	657	9.25×10^{-5}	4.49×10^{-5}	573×10^{-38}	7.31×10^{10}
Water...	3.85×10^{-8}	133.6	1.62×10^{-5}	3.84×10^{-5}	4×10^{-38}	1.39×10^{10}
Alcohol	4.96×10^{-8}	51	1.00×10^{-5}	2.31×10^{-5}	15.6×10^{-38}	0.41×10^{10}
Nitrogen	4.81×10^{-8}	41	0.78×10^{-5}	2.46×10^{-5}	6.2×10^{-38}	0.34×10^{10}

¹Vide Article II, p. 59.

These results show that molecular cohesion and adhesion is of the same order of magnitude as electrical attraction and repulsion; that it produces a pressure on the molecular mass, of the same order of magnitude as the intrinsic pressure of the liquid; and that, in comparison with it, gravitational attraction is inconceivably small.

Summary.—1. Surface tension forces have the property of uniting when the surfaces in which the tensions exist come into contact.

2. The force causing small visible liquid spheres and metal discs to adhere to liquid and solid surfaces is a surface tension force acting only in the periphery of the contact area.

3. Molecular cohesion and adhesion are of the same nature.

Theory of Forces.—It is generally assumed that all motion in the physical world results from the action of forces and, further, that these forces are limited to attractive forces, that is, they produce motion along a straight line joining the centres of two masses. The magnitude of the force is supposed to be a function of the distance between the two centres. This conception of force, however, limits its action to only one of the three magnitudes of space, namely, to linear space. Whatever theories may be employed to explain the forces of surface tension and of pressure, or whatever means may be employed to measure them, the effect of their action as observed under natural conditions is not linear in any sense of the word. The effect of surface tension (as observed about a drop of water) is to diminish the enveloping area, and the effect of pressure is to diminish the volume to which it is applied. Logically, it would be as futile to attempt to explain these latter forces in terms of attractive forces as it is to explain area and volume in terms of length. For, while lines may or must be the boundaries of areas and areas must be the boundaries of volumes, areas are not lines and volumes are not areas but in each case are essentially unlike in their nature. This may be illustrated further as follows:—

Mechanical work may be done in three ways: (1) when an attractive force changes a distance, (2) when surface

tension decreases an area, and (3) when a pressure lessens a volume. Mathematical language enables these general statements to be restricted to equations between the measures of these magnitudes thus:

$$dW = F \cdot dx \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$dW = \sigma \cdot dA \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$dW = P \cdot dV \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now the theory of dimensions shows that, since dW , or change in energy (work done), is of the same dimensions in the three cases but that dx , dA and dV are respectively of one, two and three dimensions, in line space, the corresponding force functions F , σ and P differ in linear dimensions decreasing in order by unity. This shows that fundamentally these three forces are unlike in their nature.

It is true that by restricting the action of surface tension to produce motion in one direction only (allowing it to pull on a straight line one centimetre in length perpendicular to it) it may be balanced against a linear force and measured in this restricted sense in dynes; and that by confining the action of pressure to one direction only (allowing the change of volume to take place in a strong containing chamber of fixed cross section) it may likewise be balanced against an attractive force and measured in dynes. But these restrictions are artificially designed for the sole purpose of measuring these forces and cannot affect their fundamental nature, of which we know very little.

The preceding analysis indicates then that surface tension is a fundamental force explainable only in terms of its own action and that it is incapable of explanation in terms of molecular attraction or of any other linear force.

Two results follow at once from this view. First, the various theories which in the past related surface tension to the class of attractive forces are futile and, secondly, surface tension as commonly observed must be resolvable into an element of the same nature simple and universal throughout the physical world. That this can be done may be shown

by quoting two paragraphs from a letter by the writer on *Capillarity in Nature*, Vol. 110, p. 377, 1922.¹

"If a mass consisting of a single molecule exists at all, it has a position in ether-space at some particular instant. It may be considered isolated from all other masses. There is, therefore, a closed boundary within which there are properties differing from those not within this boundary. Any part of this closed boundary may be conceived of as an area between space-regions called 'mass' and 'no-mass.' If we say that *this enveloping area tends to become less* we have defined a force which cannot be included in the class of attractive forces. Further, if we say that, *when two such enclosures come into contact the tendency to decrease does not exist in the area of contact*, since there is no distinction of properties on opposite sides of this area, we have defined the law of the force for like masses. Finally, if we say that *when two masses are unlike there is this distinction of properties and, consequently, a tendency of the common area to decrease*, we have extended the law to unlike masses." . . .

This in effect ascribes to an isolated molecule or monatomic atom a fundamental property of a definite nature which accounts for the various molecular phenomena commonly observed, including those described in the former part of this paper. The importance of this new point of view for studying phenomena is evident and the following description of the action of the force may prove useful.

All free surfaces, both liquid and solid, possess a contracting tendency which acts not within one or two layers of molecules but on the continuous exterior surface of the molecules themselves. On the free surface of an isolated molecule it pulls against itself tangentially at every point on that surface. It pulls on both sides of the thinnest possible films and causes small perforations to appear and to enlarge rapidly in a circular form. It alone causes all liquid particles, from molecular sizes up to the dimensions of rain drops, to be

¹Vide Article III, p. 61.

spherical, as well as the segregated masses of one constituent of a liquid solution or emulsion. It acts with different intensities about the free molecules of different substances but otherwise it is of the same nature. Consequently, whenever two free surfaces come into contact, the two forces unite instantaneously at the perimeter of the contact area and form a continuous contracting tendency enveloping the two masses, which are thus bound together into one and which are rapidly changed into one spherical form. All visible liquid spheres coalesce in this manner, and they may be observed to do so in the case of mercury. It is difficult to deny that they refuse to do so when they are beyond visible sizes down to the molecules themselves. The attachment of mercury to a clean glass surface and the coalescence of the spheres by lateral contact is a true picture of the condensation of mercury vapour on the sides of its containing vessel and of a gas of any kind upon a solid surface.

Further, all free surfaces possess potential surface energy by virtue of the surface forces being in equilibrium. In any case where these forces are not in equilibrium work will be done until a minimum area is reached. All cases of contact, therefore, are attended by the conversion of potential surface energy into an equivalent amount of heat energy. This is the source of the latent heat of a gas. No molecule can be separated from its fellow or from a mass in liquid or solid form without the addition of energy necessary to form the new surface. Inside a pure liquid no such force surrounds the molecule, which may be of any shape depending upon other interior forces, but when it is ejected through the exterior surface of the liquid its own free surface must be given its store of potential surface energy equal in amount to the energy of projection. The way in which a molecule is separated from its liquid is the same as the way in which a visible drop is separated. Unlike molecules, when they come into contact, unite by their surface forces and remain attached, unless their relative velocity of impact was too great. A true molecular solution may change into a colloidal solution

by the molecules of one of the constituents coalescing into larger masses of a visible size.

The experimental evidence upon which the foregoing statements are based may be classified as follows:

(1) All visible liquid spheres of like liquids coalesce on contact regardless of their absolute or relative sizes and of the kind of liquid. No exception has been observed. The significance of this universal phenomena is shown in a paper on "*The Coalescence of Liquid Spheres—Molecular Diameters.*"¹

(2) All visible spheres of unlike liquids coalesce on contact and in most cases immediately assume a spherical form, the one liquid surrounding the other completely.

(3) All liquid and solid particles of whatever kind attach themselves to each other on contact and create a permanent interfacial area. The former part of this paper shows experimentally that the cohesive force causing the attachment is a surface force acting at the perimeter of the interfacial area and is not, as is generally supposed to be the case, due to molecular attraction across the contact area.

(4) All solid particles of whatever kind if sufficiently small but quite within the range of visibility attach themselves to one another and to solid surfaces so firmly as to resist powerful efforts to separate them.

In conclusion the writer hopes to publish soon another paper with special reference to the phenomena of internal cohesion in liquids and solids, in which experimental evidence will be brought forward to show that the force of molecular tension is the controlling force in the molecular structure of various solids.

¹Vide Article I, p. 24.

ARTICLE VI

COHESION IN LIQUIDS AND SOLIDS

The writer recently defined¹ a physical force which does not admit of being classed with those known as attractive forces and stated the laws by which it operates. More generally the force is defined in the statement: *the common area of two contiguous space regions possessing unlike mass properties tends to become less*. It follows that an isolated molecule is subject to this force (molecular tension), that is, its enveloping area tends to a minimum; that the force is absent in the common area of two like molecules in contact while acting in the area about the combined mass (law of molecular cohesion); and finally, that the force, in diminished strength, is present in the common area of two unlike molecules in contact (law of molecular adhesion).

Experimental evidence of the operation of this force as a primary cause of molecular phenomena has been brought forward in a number of papers in which it is shown that the conception of the force and its laws offers a satisfactory explanation of surface tension and latent heat of a gas,² cohesion and adhesion as observed externally,^{3, 4} and capillarity and fluid spreading over liquid and solid surfaces. The present paper is an attempt to explain on the same basis the phenomena of cohesion as observed in the interior of liquids and solids.

General Properties of Cohesion.—It is generally recognized that, whatever be the nature of cohesive force, the effect of overcoming it is located in the molecular surfaces themselves; for, when solids are broken apart, we deal only with an intermolecular and not an intramolecular cleavage, that is to say, the force does not produce or depend on any change in the

¹"Capillarity", *Nature*, Vol. 110, p. 377, 1922 (Article III, p. 61).

²"Coalescence of Liquid Spheres—Molecular Diameters", *Phil. Mag.*, Vol. 41, p. 877, 1921 (Article I, p. 24).

³"Cohesion", *Nature*, Vol. 109, p. 413, 1922 (Article IV, p. 66).

⁴"Cohesion and Adhesion", *Phys. Rev.*, p. 413, April, 1922.

constitution of the molecule or of the atomic masses themselves and is a purely physical force as opposed to chemical or electrical forces. There appears, also, to be no question that the number and orderly arrangement of the atoms in the molecule determine in a large measure the forms of the molecular surfaces that are in contact when the molecules orient themselves into crystals.

In a liquid, however, the atoms making up the molecule appear attached to one another in such a way as to allow the molecular surface to change its form and extent freely while the molecular volume is constant; and, consequently, the molecular surfaces in contact may adjust themselves freely to exterior conditions. Any attempt, then, by purely mechanical means, to separate two such surfaces in the interior of a liquid would be of no avail on account of the distribution of the applied force to other parts of the liquid. Cohesion may therefore be regarded as the force which resists molecular separation; and it is generally thought of as opposing another force referred to as intrinsic pressure which would cause molecular separation.

It is proposed to give in the following pages experimental evidence to show that the work done in this case by the impressed force upon the system is precisely equal to the potential energy stored in the free surface of the ether cavity created; and that, when a molecule is separated from its liquid into free space, the work done is equal to the potential surface energy of the free molecule.

Measure of Cohesive Force.—If Laplace's law of pressure be applied either to this molecular ether cavity in the liquid mass or to a molecular mass isolated in space, we get

$$K = \pm \frac{4\sigma_0}{d} \dots (1)$$

where K is either the intrinsic pressure or the cohesive force, σ_0 , the molecular tension, d , the diameter of the sphere, and \pm indicates the opposite directions of these two forces—the intrinsic pressure tending to enlarge and the cohesive force tending to reduce the molecular volume.

It may be remarked that, since K is the measure in dynes per square centimetre of surface and σ_o in dynes per centimetre of length, these forces differ from each other in their nature in the same way as space in two dimensions differs from space in one dimension; and just as a magnetic force is said to be induced by an electric current and is proportional to it, so it may be said that the cohesive force is induced by molecular tension and is proportional to it, while, in either case, the induced force is different in nature from the primary cause.

Equation of Condensation.—From the fact that the coalescence of visible liquid spheres takes place, without any observed exception, according to the law of the force defined above, the writer has shown that the law of coalescence is expressed by the equation,

$$n = \left(\frac{LJ}{\sigma} \right)^3 \times \frac{m\rho^2}{36\pi}, \quad (2)$$

where n is the number of spheres that coalesce to form a gram molecule of the liquid, L the surface energy in calories per gram mass of the spheres, σ the surface tension, ρ the density of the liquid, and m the molecular weight. There is no *prima facie* reason to believe that the spheres will cease to coalesce when they are below the range of direct vision and, consequently, that the equation should not hold for molecular spheres. If, then, the equation holds true up to this limit, it becomes the equation of change of state applicable in all cases when a substance changes from a liquid to a gaseous state and vice versa. It may then be written:

$$N = \left(\frac{L_o J}{\sigma_o} \right)^3 \times \frac{m\rho_o^2}{36\pi}, \quad (3)$$

where N is Avogadro's number, L_o the latent heat in calories of a gram mass of the gas under zero pressure, that is, excluding the work done against vapour pressure, σ_o the molecular tension, and ρ_o the molecular density. It may also take the form,

$$m\rho_o^2 L_o^3 = A \sigma_o^3, \quad (4)$$

where A is an arithmetical constant $= 36\pi N/J^3$.

Calculation of d and K .—The writer has also shown that the diameter of the molecule may be obtained from the equation

$$d = \left(\frac{mL_o J}{\pi \sigma_o N} \right)^{\frac{1}{3}}, \quad \dots \quad (5)$$

When L_o/σ_o is replaced in this by its equivalent in equation (3), the ordinary equation of the molecular diameter is obtained:

$$d = \left(\frac{6m}{\pi \rho_o N} \right)^{\frac{1}{3}}, \quad \dots \quad (6)$$

whence also

$$d = \frac{6\sigma_o}{\rho_o L_o J}, \quad \dots \quad (7)$$

When these values are written for d in equation (1), three equations for determining K are obtained:

$$K = \pm 4 \left(\frac{\pi \sigma_o^3 N}{m L_o J} \right)^{\frac{1}{3}}, \quad \dots \quad (8)$$

$$K = \pm 4 \sigma_o \left(\frac{\pi \rho_o N}{6m} \right)^{\frac{1}{3}}, \quad \dots \quad (9)$$

and

$$K = \pm \frac{2}{3} \rho_o L_o J, \quad \dots \quad (10)$$

It is thus possible to calculate both the diameter of the molecule and the cohesive force when any two of the three quantities L_o , σ_o , and ρ_o have been determined experimentally.

History of Cohesion—In his *Theory of Surface Forces* Rayleigh¹ calls attention to the first estimate of intrinsic pressure made by Thomas Young² in 1805, and also to an idea which originated with Dupré³ more than sixty years later, that the intrinsic pressure should be roughly equal to the latent heat of dissociation. Rayleigh regarded Dupré's principle as "substantially sound", and from the equation,

$$K = LJ,$$

by putting $L = 600$ calories, obtained for water $K = 25,000$

¹*Phil. Mag.*, Vol. 30, p. 473, 1890.

²*Collected Works of Thomas Young*, Vol. I, p. 461.

³*Théorie Mécanique de la Chaleur*, 1869, p. 152.

atmospheres; while Dupré by taking $L = 550$ calories obtained 23,000 atmospheres. It will be seen that the equation of Dupré and Rayleigh differs from equation (10) only in lacking the factor $\frac{2}{3}\rho_0$. Young's determination of K is contained in the words: "Now there is reason to suppose the corpuscular forces of a section of a square inch of water to be equivalent to the weight of a column 750,000 feet high". This gives $K = 22,300$ atmospheres which agrees closely with Dupré's value.

Rayleigh also points out that Young used this value to find the first estimate of the range of molecular attraction. Young conceived, intuitively as it seems, that the tension of a liquid should be $\frac{1}{3}$ of the intrinsic pressure exerted through a distance r , the range of molecular attraction; that is, he conceived the relation $\sigma = \frac{1}{3}Kr$. If, however, r be taken as the distance between the centres of two adjacent molecules in the liquid, r may be changed to d and Young's equation may be written

$$\frac{1}{3}K = \frac{\sigma}{d}$$

which differs from equation (1) only in having the fraction $\frac{1}{3}$ instead of $\frac{1}{4}$. Rayleigh thinks, however, from his own calculations that Young's fraction should be $3/20$.

Since equations (10) and (1) are connected by means of equation (3) it will be observed that these two apparently independent equations conceived by Young and Dupré connecting K with surface tension and latent heat are in reality identical. Rayleigh further points out that the distinction between force and energy had not then been made and was unknown to these two writers, and it may be well in this connection to refer to it again. Just as σ , which is the measure of surface tension (force) in dynes per centimetre of length, is also the measure of surface energy in ergs per square centimetre of surface, so K , which is the measure of intrinsic pressure in dynes per square centimetre of surface, is also the measure of intrinsic energy in ergs per cubic centimetre of

volume. It is probable that Young thought of K in the former sense and Dupré in the latter.

More recently the problem has been investigated by A. P. Mathews.¹ He adopts as his basic idea that K is the term a/V^2 in van der Waals' equation of state $(P - a/V^2)(V - b) = RT$. Instead, however, of adopting van der Waals' method of obtaining the value of a/V^2 by direct observations at the critical state, he reverts to Young's formula, $\sigma = \frac{1}{3}Kr$, considering the value of obtained from surface tension measurements to be "more trustworthy" than that obtained by any of the various methods followed by other investigators of van der Waals' equation. His chief difficulty lies in estimating r . In an earlier paper² in which he takes $v = V/N$ he says, "we may safely assume that $r = v^{\frac{1}{3}}$ " where " v is the space at the disposal of one molecule at absolute zero." This leads him to consider "the molecular surface tension energy at absolute zero"; but he fails to notice that this conception necessarily implies the conception of molecular surface tension. Had he done so, his molecule would have been spherical rather than cubical and r would have been $(6vk_1)^{\frac{1}{3}}$ or d instead of $v^{\frac{1}{3}}$. Now the determination of v involves that of ρ_0 . He then assumes with van der Waals that $\rho_0 = S\rho_c$ where $S = RT/PV$, the suffix c referring to determinations at the critical point. For some liquids he finds that S differs but little from 4 and he assumes this to be the case with the others. But not having ρ_c for many substances he is unable to calculate ρ_0 , and, consequently, his determinations for K are limited to seven. For some reason he expresses no opinion as to whether van der Waals' value of 11,000 atmospheres is to be preferred rather than that of Young in the case of water.

Meaning of the Symbols.—In these equations for the diameter of the molecule it is assumed that at absolute zero the molecules possess no individual motions and that they constitute the mass in such a way that there is no intermolecular space; and thus ρ_0 , which is the density of the whole mass at 0° A., is also the molecular density. Likewise, each molecule

¹Various papers, *Jour. Phys. Chem.*, Vol. 17, 1912.

²*Idem*, pp. 156-7.

occurs is compensated for by the sudden increase in ρ_T during in the surface of the whole mass at 0°A. , being without motion, contributes an integral part of the enveloping area and, consequently, σ_0 , which is the surface tension of the whole mass at 0°A. , is also the molecular tension. Now, as absolute zero has never been, and probably can never be, attained, the absolute values of ρ_0 and σ_0 may never be experimentally determined. They are greater than ρ_T and σ_T where T° denotes the lowest absolute temperature at which ρ and σ have been determined. On the other hand, L_0 being the latent heat of molecular dissociation of a gram mass at zero pressure is capable of exact determination. It is precisely equivalent to the potential energy stored in the free surfaces of the dissociated molecules and is equal to the difference in calories between the total latent heat at the boiling point and the work done against the pressure of its own vapour equal to $R.T_{B.P.}/mJ$ calories. In all calculations $N=6.065 \times 10^{23}$ (Millikan's value) and $J=4.184 \times 10^7$.

Tables. The following Tables I and II contain the values of ρ_0 , σ_0 , L , d , and K , which satisfy the equations (1) to (10). Table I includes sixteen metallic and five gaseous chemical elements, while Table II comprises sixteen of the more common liquid compounds. They include, also, for comparison some values determined by other investigators who employed independent methods. The sources from which the accepted values of the physical constants were obtained are indicated.

Determination of ρ_0 .—Experimental evidence goes to show that except when the substance is near the melting point $\frac{d\rho_T}{dT}$ for the liquid or solid state is approximately constant; that, except in the case of water, ρ_T suddenly becomes larger when the substance becomes solid; and that $\frac{d\rho_T}{dT}$ is less for the substance in the solid than in the liquid state. If, then, it be assumed that the lesser value of $\frac{d\rho_T}{dT}$ after solidification

this change of state, ρ_0 will be very approximately obtained by considering the observed value of $\frac{d\rho_T}{dT}$ for the liquid to hold down to absolute zero. This method of extrapolating for ρ_0 has been adopted whenever sufficient data were available. It appears to be preferable to that of van der Waals of estimating ρ_0 as four times ρ_c , which Mathews adopts with modifications. Besides, the method of extrapolation is applicable in all cases, while the method of the critical data is for many substances impossible on account of the high temperatures involved. This is the case with the metals where no change of state occurs and fairly accurate results may be expected. In the following Tables I and II the extrapolated values of ρ_0 are given along with those of ρ_T observed at the lowest temperature T° . In a few cases, however, where the data were insufficient the observed value ρ_T is repeated as ρ_0 .

Determination of σ_0 and L_0 .—Since only one of the quantities σ_0 and L_0 is required for the calculation of d and K , L_0 has been selected whenever possible in preference to any extrapolated value for σ_0 , as being less subject to error. The value of σ_0 was calculated by means of equation (3) or (4). The values of either σ_0 or L_0 calculated by this means are enclosed in brackets. It will be seen that the calculated value for all the substances except toluene and hydrogen is greater than the greatest experimental value¹ at the lowest recorded temperature. This is in accordance with the law of increasing tension with decreasing temperature. The values obtained at the lowest temperatures are given for comparison. Again, it was found that these values calculated by equation (3) are in general less than the values (not given in the tables) found by extrapolation by considering $\frac{d\sigma_T}{dT}$ constant down to 0°A . For water these values are equal. The exceptions are the cases of mercury and the three alcohols where the extrapolated values are less than the

¹*Tables internationales* (1921), p. 201 *et seq.*

others. It is possible that these exceptions may be due to errors of observation and the difficulty of obtaining chemically pure alcohols. A redetermination of the latent heat of mercury is desirable where precautions are taken to ensure monatomic dissociation of the vapour.

For the metals, however, the surface tensions only are available, the latent heats, except that for mercury, being obviously beyond experimental possibility. Though these values of σ_T having been determined at the high temperatures of the molten state are considerably less than the molecular tensions, they have been used in equation (3) to calculate the latent heats of the metallic gases and in consequence L is proportionately less than the true energy of dissociation of the molecules. The greater number of these surface tensions were determined in the laboratories of the Royal Mint by Sydney W. Smith¹ in 1914. His method, which consisted in measuring the depression of the molten metal in capillary tubes of carbon and which was perfected so as to give consistent results, is considered more reliable than that of Quincke, who weighed the drops as they fell from a vertical wire of measured diameter fused in a hot flame, or that suggested by Quincke and adopted by others of obtaining the surface tension from the weight and curvature of a molten drop after it had cooled on a horizontal plane.

For comparison the theoretical values of the latent heats of vaporization of the elements which were determined by Richards² are also given in Table I. They agree with those calculated by equation (3) but are in general greater, as would be expected for the reason given above.

Hence, with few exceptions, all of which are capable of explanation, the equation of condensation (3) is satisfied with consistent experimental values of ρ_0 , σ_0 , and L_0 for all substances of which the necessary data are available. These substances range, in the elements, from platinum to hydrogen

¹"Surface Tension of Molten Metals", *Jour. Inst. Metals*, Vol. 12, p. 201, 1914.

²*Smithsonian Tables*, p. 233, 1920.

TABLE I—Elements

	m	ρ_T	T°	ρ_o	σ_T	T°	σ_o	L_o	$d \times 10^8$	$K \times 10^{-6}$	Traube ⁵ $K \times 10^{-6}$	Richards ⁷ $L_o = L - \frac{RT}{mJ}$
Platinum.....	195.2	21.5	2000	21.5	1691	2000	1691 ¹¹	(369)	3.13	221,000	324,200	292
Gold.....	197.2	18.38	1393	19.62	1018 ⁶	1393	1018 ²	(235)	3.18	128,700	178,500	302
Silver.....	107.88	9.543	1273	10.20	858 ⁶	1273	858 ²	(375)	3.22	85,840	161,900	448
Copper.....	63.57	8.32	1423	9.08	1178 ⁶	1432	1178 ²	(664)	2.80	168,100	236,100	788
Nickel.....	58.68	8.9		8.9	1538 ⁶		1538 ²	(899)	2.75	223,900	306,300	919
Iron.....	55.85	7.86		7.86	1244 ⁶		1244 ²	(806)	2.82	176,600	239,000	1015
Aluminium...	27.1	2.65		2.65	520 ⁶		520 ²	(855)	3.18	65,370	119,300	
Lead.....	207.1	10.51		11.99	424 ⁶		424 ²	(134)	3.79	44,680	51,100	210
Zinc.....	65.37	5.81		7.71	707 ⁶		707 ²	(440)	2.99	94,910	108,900	395
Tin.....	119	6.66	950	7.56	480 ⁶	950	480 ²	(248)	3.67	52,260	68,900	439
Bismuth.....	208	9.77	1100	9.81	346 ⁶	1100	346 ²	(125)	4.06	34,120	97,300	174
Antimony...	120.2	6.45	1120	6.71	274 ⁶	1120	274 ²	(153)	3.84	80,240	117,700	329
Potassium...	39.1	.862		.862	371		371 ¹¹	(1181)	5.23	28,390		544
Sodium.....	23	.971		.971	258		258 ¹	(905)	4.21	24,520		1069
Cadmium.....	112.4	8.64		8.64	824		824 ¹	(397)	3.45	99,140		213
Mercury.....	200.	13.645	252	14.26	554	273	650	(185)	3.54	73,550		68
Argon.....	39.88	1.4	88	1.4	13.45 ³		17.6 ⁸	(40.8)	4.45	1,604		183
Chlorine.....	70.92	1.717	173	2.10	21.9 ³	273	(41.8)	60.3 ⁴	4.63	3,532		74
Oxygen.....	32	1.14	77	1.14	13.1 ⁴	90	(16.5)	47.5 ⁴	4.37	1,510		56
Nitrogen.....	28	.81	90	.81	8.5 ⁴	77	(11.1)	41.0 ⁴	4.78	927		58
Hydrogen.....	2	.0771	13.8	.0904	3.18 ³	16.6	(2.78)	107 ⁴	4.11	270		

TABLE II—Compounds

	<i>m</i>	ρT^3	T^{03}	ρ_0^8	σT^3	T^0	σ_0	L_0^4	$d \times 10^8$	$K \times 10^{-6}$	Mathews ⁶ $K \times 10^{-6}$
Toluene.....	92	.956	202	1.162	43.7	202	(38.6)	75.7	6.29	2454	2534
Benzene.....	78	.895	278	1.239	30.9	278	(41.3)	81.9	5.83	2831	2946
Car. bisulphide.....	76	1.398	201	1.694	44.3	201	(46.5)	75.5	5.21	3568	3937
Car. tetrachloride.....	153.8	1.659	255	2.127	30.9	255	(38.1)	42.1	6.11	2498	2637
Ethyl acetate.....	88	1.016	199	1.265	36.6	199	(42.3)	79.6	6.03	2808	2507
Ethyl ether.....	74	.818	198	1.036	28.5	198	(37.9)	86.2	6.08	2491	1986
m-Xylene.....	106	.873	285	1.117	29.7	285	(42.7)	83.3	6.59	2594	2228
Acetone.....	58	.917	200	1.176	35.6	200	(50.2)	113.8	5.38	3734	
Acetic acid.....	60	1.046	299	1.148	27.0	299	(32.1)	72.2	5.48	2312	
Chloroform.....	119	1.555	251	1.979	32.5	251	(42.1)	53.1	5.74	2932	
Aniline.....	88	1.038	273	1.367	45.4	273	(61.6)	110	5.88	4203	
Turpentine.....	136	.956	199	1.129	35.8	199	(67.7)	67.7	7.24	2131	
Water.....	18	1.000	277	1.000	75.6	273	(133.7)	498	3.85	13900	
Ethyl alcohol.....	46	.886	194	1.064	30.6	194	(81.3)	213	5.14	6324?	
							47.0 ⁸	(123)		3658	
Methyl alcohol.....	32	.878	198	1.056	29.8	198	(89.7)	267	5.57	7865?	
							45.4 ⁸	(135)		3981	
Propyl alcohol.....	60	.881	197	1.047	33.4	197	(68.2)	165.3	5.65	4827?	
							51.6 ⁸	(125)		3651	

¹Quincke, *Smithsonian Tables*, p. 174, 1920.²Smith, *Jour. Inst. Metals*, Vol. XII, p. 201, 1914.³*Tables Internationales*, 1913-1916, p. 99 *et seq.*, 1921.⁴Kaye and Laby, *Physical and Chemical Constants*.⁵Smith, *Jour. Inst. Metals*, Vol. XVI, p. 71, 1917.Traube, *Ber. deut. phys. Gesellsch.*, pp. 231-236, 1909.⁶Mathews, *Jour. Phys. Chem.*, Vol. 17, p. 627, 1913.⁷J. W. Richards, *Smithsonian Tables*, p. 233. External work deducted.⁸Extrapolated from data in *Tables Internationales* (1916) p.12.

and in the compounds include the common liquids. The latter list may be greatly increased as new data become known.

Heats of Molecular Dissociation of the Metals. Excepting mercury it is perhaps impossible to obtain experimental values for L for the metals on account of their high boiling points. The values (in brackets) for eleven of the metals are those obtained by means of equation (5) from σ_T where T° is the lowest temperature for which values of σ are available. For the other five, the extrapolated values of σ were used. Except for mercury the values of σ_T are likewise used instead of those of σ_o . It is quite certain that σ_o does not greatly exceed σ_T , while L_T , although there are no available data for its calculation, is without doubt considerably greater than L_o . These considerations indicate that the true values of L are in general greater than those calculated in Table I. This is borne out by comparing these values with those calculated by Richards from different data (Smithsonian Tables, p. 233, 1920.) With the exceptions of mercury and potassium the correspondence is very close. The correspondence also holds fairly well between Richards' theoretical values and the actual determinations of Young (1910) for chlorine, oxygen and nitrogen.

Molecular Tension in Compounds. In Table II the values of L are chiefly those determined by Young and it is considered that the values of σ_o calculated from these and ρ by equation (5) are more reliable than those found by extrapolation from observed values of σ . For comparison the greatest of these latter are given. With one exception only they are, as was to be expected, less than those determined by equation (5). In this case, however, L for toluene was determined by Brix in 1842 and is not included in those determined by Young. The values of ρ , determined by extrapolation, except for the alcohols, are not given in Table II, but they are, with these exceptions, greater than those calculated by equation (5). In the case of water the values of ρ determined by extrapolation and by equation (5) are equal. In the case of the three alcohols the extrapolated values are less than

those determined by equation (5), which leads one to think that Young's latent heats for the alcohols are too high.

Table II also contains the seven determinations for K by Mathews. They are in remarkable agreement with those calculated by any of the equations (7) to (10).

Crystalline Structure of Metals and the Spherical Diameters of their Atoms in the Gas Phase. By the method of X-ray analysis, discovered by the Braggs, nine of the metals in Table I have been found to crystallize in the cubical structure, that is, atomic centres are situated at the corners of a cube and one either at the centre of the cube or at the centre of each face. In one other metal, zinc, the atomic centres are found at the corners and three centres in the interior of a regular hexagonal prism whose axis is 1.633 times a side of the hexagon. The nature of the boundary separating adjacent atoms is not yet determined, since no means has been found of rendering that boundary evident to our senses. Nevertheless, when the crystal structure breaks down by the application of heat, we may suppose that the atomic centres become disarranged and the forms of the atoms are no longer fixed. On changing to the gas phase the atoms or monatomic molecules are completely separated from one another. Their surfaces are then endowed with the properties of molecular tension and potential surface energy, and probably have the power of scattering visible light. If we assume that the atom suffers no change in volume during these changes of phase, the corresponding spherical diameters may be calculated from the atomic spacing. For the body-centred cube $d = (3/\pi)^{\frac{1}{3}} a$, and for the face-centred cube $d = (3/2\pi)^{\frac{1}{3}} a$, where a is the edge of the cube. For the hexagonal prism $d = (1.633 \times 3\sqrt{3}/2\pi)^{\frac{1}{3}} a$, where a is a side of the hexagon. These are calculated in Table III and compared with the spherical diameters of Table I.

TABLE III
DIMENSIONS IN 10^{-8} CM.

Substance	Edge of F.C. cube	Edge of B.C. cube	Side of hex. face	Diam. of equal sph. atm. vol.	Atomic diam. in Table I
Iron.....		2.86		2.82	2.82
Sodium....		4.30		4.23	4.21
Aluminium..	4.05			3.22	3.18
Nickel.....		2.73		2.72	2.75
Nickel.....	3.52			2.75	2.75
Copper....	3.63			2.84	2.80
Lead.....	4.95			3.87	3.86
Platinum...	4.02			3.14	3.13
Gold.....	4.08			3.19	3.18
Silver.....	4.06			3.17	3.22
Zinc.....			2.84	3.14	3.04

These results confirm in a remarkable degree not only that the atom or monatomic molecule conserves its volume through its changes of phase, but also that the equation of condensation (5) is true for the metals.

Cohesive forces.—It may be remarked that, if in an amorphous or crystalline solid the atoms in the molecule are held in such a condition as to render the molecule absolutely fixed both as to its form and volume, it is difficult to see that a stress could be powerful enough to cause a molecular separation. For, in such a case a large extent of free surface would have to be instantaneously stored with potential energy, that is, work would have to be performed at an infinite speed. This is impossible. It appears, then, that the hardness of solids depends jointly on the cohesive force between the molecules and on some other force or cause within the molecule by which the atoms are made to arrange themselves in fixed positions.

Consider the faces of two atoms supposed cubical to be in contact. If these be separated, the work necessary to create the new free surface, $dA = 2a^2$, would be a definite quantum, $dE = 2\sigma a^2$, where a is an edge of the cube. But if the cubes were absolutely rigid the separation would occur in time $dt = 0$,

and, consequently, dA/dt would be infinitely great, that is, the time rate of change of energy (power) would be infinitely great. This is contrary to the thermodynamical law. In this case also the applied force which would cause the separation would be infinitely great. If, however, the interior forces of rigidity of the atom allow a deformation so that the separation may begin at a point and gradually extend over the whole area of contact, both dA/dt and dE/dt would be finite and the separation possible.

Before, however, the applied force begins to form new surface it does work against the interior forces of rigidity and stores up potential energy by producing a state of strain by balanced forces increasing to a certain maximum in the atoms themselves. This potential energy is very much greater than that necessary to create the new surface, and as soon as the surfaces begin to separate the original forms begin their restoration and the excess of energy is transformed into heat. This explains the elastic properties of metals and the production of heat when they are hammered or abraded.

There is, however, in all solids, when the mass is subjected to great stress, a certain amount of deformation and change in molecular volume which permits the formation of intermolecular cavities with curved areas. In such a case we may suppose that before an actual separation occurs a slight enlargement of the molecular volume, accompanied by a displacement of the atomic masses in the molecule, takes place under the stress, and that when the stress at its maximum overcomes the cohesive force and produces a cleavage of sensible extent, the molecules suddenly revert to their original shape and volume. This would account for the elastic properties of solids and would also explain the occurrence of violent shocks which cause the vessel in which a liquid is being raised to the boiling point to emit a musical note.

But the most striking confirmation lies in the agreement of the values of the cohesive force with those obtained by Mathews in the case of seven of the liquids, and by Traube for the principal metals. In one respect the methods em-

ployed by these investigators are similar. Both based their reasoning on van der Waäls equation of state which assumes a continuity of properties between the liquid and gaseous states. This continuity may be explained. When a liquid is near the critical point, the ether cavities in the liquid multiply and by coalescence are joined into larger cavities. Through the walls of these cavities molecules more or less associated by coalescence are projected into the free ether space which soon acquires the properties of a gaseous vapour. At the same time the increasing pressure causes the molecules of the vapour state to coalesce into associated groups. These two processes continue under the increasing temperature and pressure until the liquid, which now constitutes a wall structure between spherical cells, disintegrates into separate spherical molecular groups and becomes similar in constitution to the vapour state while the meniscus disappears from view. The surface tension, however, still remains about the spherical liquid masses as is evidenced by the scattering of light by the substance in these changing phases. It would be expected, then, that the statistical equation of van der Waäls would give results similar to those obtained by the equation of coalescence. Mathews, however, as was pointed out, considers the cohesive forces derived from surface tension measurements to be more reliable than those from the critical data.

Traube¹ assumed that van der Waäls' equation held true for the solid state, and by using the compressibilities of the elements which were now available through the work of Richards² and his collaborators at Harvard obtained values of the cohesive force a/V for the principal metals and a number of other substances. He found that for 14 of the metals in their solid state the cohesive force approximately varied inversely as the square root of their atomic compression. His values for K are given in Table I. They show a remarkable correspondence with those calculated from the molecular densities and surface tensions by means of the equations given

¹*Jour. Chem. Soc.*, 2, pp. 216, 550, 1909.

²*Carnegie Inst. Publs.*, No. 76, 1907. *Jour. Am. Chem. Soc.*, 36, p. 2417, 1908.

above except that for the reason given previously they are in general greater than the latter.

Smith, in a later paper,¹ compared his own values of the surface tensions of the metals with Traube's values of their cohesive forces and was able to say that "a relation has been shown between surface tensions of molten metals . . . and the internal pressures . . .", though he was unable to formulate this relation.²

¹"Surface Tension and Cohesion in Metals and Alloys", *Jour. Inst. Metals*, p. 651, 917.

²This is not strictly correct. Smith gives the following equation:—
Surface tension = (Int. press. $\times 10^{-2}$) $\times 0.427 + 200$.—(Edit.).

ARTICLE VII

THE POTENTIAL ENERGY OF THE FREE MOLECULE

I

In a former article it is shown that the conception of a force-area or area-force about every free molecule of any liquid followed logically from the well-known universal phenomenon of the coalescence of two liquid drops of any substance when brought into contact. There is a strong presumption, amounting almost to a proof, that such a conception is that of a universal fact of nature. If so, then every free molecule or atom of any substance possesses this area-force about it as an essential property by which the phenomena of the interior mass is separated from the exterior phenomena of ether space. The molecule, or atom, thus adds the properties of its own mass to those of the ether space, and the force enclosure marks the boundary of such addition. It is this area-force which determines in a great measure the form of the free molecule, which is thus probably spherical.

But the consequence of such a conception is another conclusion, that each free molecule, or atom, carries its own definite load of potential energy, which, as long as the molecule remains free, cannot be released to do work. This energy is quite distinct from the kinetic energy of the molecule, or atom, which is measured by $\frac{1}{2}mv^2$, and which is therefore a function of its mass and velocity. It is not a function of either mass or velocity; it is a function of tension and area and is measured by $T \times A$. The tension depends, not on the mass, but on the inherent properties of the substances themselves, in such a way that different substances possess tensions of different intensities.

This potential energy thus carried by the free molecules of a gas is the "hiding place" of the latent heat of condensation, and becomes apparent when the gas condenses to a liquid. Each gas then possesses a definite amount of potential energy quite independent of its temperature. Thus, the gram

mass of pure steam possesses 495 calories of potential energy, that of oxygen 47 calories, that of nitrogen 39 calories, and that of carbon dioxide 48.2 calories.

Now the only way nature has of releasing this potential energy is to cause the molecules to come into contact with each other under such conditions that coalescence is established.

Let ρ = the density of the liquid.

d = the maximum average diameter of the molecule in its liquid condition.

d' = the minimum diameter in gas.

d'' = the diameter determined by other methods (J. H. Jeans).

T_u = the measured tension of the liquid at 17° C.

T' = the mean tension calculated as below.

C = the latent heat of condensation corrected for external work.

θ° = the absolute temperature of the boiling point.

m = the relative weight of the molecule.

E = the potential energy carried by one molecule.

N = Avogadro's number = 6.065×10^{23} .

The values of d , d' , T' and E in the table below have been calculated from the formulae previously explained as follows:

$$T' = \left(\frac{\rho^2 m}{36\pi N} \right)^{\frac{1}{3}} \cdot C \cdot J. \quad d' = d \left(\frac{T_u}{T'} \right)^{\frac{1}{2}}$$

$$d = \left(\frac{6m}{\pi \rho N} \right)^{\frac{1}{3}} \quad E = \frac{CmJ}{N}$$

where $J = 4.187 \times 10^{-7}$.

In the case of carbon dioxide the tension of the liquid surface appears not to have been determined experimentally by any one. We have predicted that it should be 7.1, and also that the latent heat of evaporation of mercury should be slightly greater than 147, if the evaporation is complete. There appears to be a slight error in the observed tension of liquid nitrogen which should be a little less than 8.2.

It will be observed that the mean tension T' as calculated, and the load of potential energy E carried by the separate molecules, both increase with the absolute temperature. This

TABLE I

	m	ρ	θ°	C	T_u	T'	$d \times 10^8$	$d' \times 10^8$	$d'' \times 10^8$	$E \times 10^{14}$
N.....	4	.79	77	39	8.5(?)	8.2	3.82	(3.82)	3.33	3.77
O.....	16	1.27	90	47	13.1	14.2	3.41	3.27	3.09	5.19
CO ₂	44	.772	195	48.2	(7.1)	14.6	5.64	(4.08)	4.08	14.6
C ₂ H ₆ O.....	46	.806	352	199	22	58	5.64	3.43	2.74	63.1
H ₂ O.....	18	1.00	373	495	74.4	133	3.84	2.88	3.77	76.7
Hg.....	200	13.6	630	(147) 62(?)	540	(540)	3.59	(3.59)		219
CS ₂	90	1.25	319	80	33.6	43.6	6.10	5.41		49.7

is consistent with the following explanation. The coalescence of two like molecules of a gas depends on two factors, namely, the magnitude of the area-force of coalescence and the velocities of impact, in such a way that an increase in the velocity of impact requires a corresponding increase in the tension of the area-force to overcome the elastic rebound. In other words, the lower the temperature of the condensing point, the less is the tension of the area-force. This is seen to be the case for the six liquids above. Further, the difference between the measured tension T_u and the molecular tension T' depends on the violence of the molecular impacts on the surface whose tension is being measured. The low temperature in the case of oxygen and nitrogen indicates a low intensity of impact, and we would expect T' to be nearly equal to T_u . In the case of mercury, even though it has a very high boiling point, yet, on account of the great density of the mercury molecule relative to those bombarding it, the difference between T' and T_u would be small.

Strange as it may seem, there does not appear to be any evidence that the coalescence of liquid drops or of free molecules is caused in any way by the attraction of their masses towards each other. For, if this were the cause, we would be unable to explain the violent jerking of the two masses of the drops together at and not before the instant of contact.

Let us first consider the drops as two masses. Then

$$F = G \frac{mm'}{x^2}$$

and therefore

$$F \cdot \delta x = G \frac{mm'}{x^2} \delta x.$$

that is,

$$\delta E = G \frac{mm'}{x^2} \delta x.$$

Now δE is sensibly finite;

$$G \frac{mm'}{x^2}$$

is also finite, x being equal to d at contact; and δx , being equal to the difference between the distances of their centres before and after contact, is vanishing. Thus we have the ratio between two finite quantities equal to an infinitesimally small quantity or zero, which is impossible.

Next, let us consider two free molecules of water in contact.

Then

$$\begin{aligned} F &= G \frac{m^2}{d^2} \\ &= 6.66 \times 10^7 \times \left(\frac{18}{6.065 \times 10^{23}} \right)^2 \div (3.84 \times 10^{-8})^2 \\ &= 2.60 \times 10^{-39}. \end{aligned}$$

Again, if F' be the binding pull of the area-force neck between the two molecules, $F' = T' \pi d'$ where d' is assumed to be approximately $\frac{1}{2}d$. Thus

$$\begin{aligned} F' &= 133 \times \pi \times \frac{1}{2} \times 3.84 \times 10^{-8} \\ &= 8.02 \times 10^{-5} \end{aligned}$$

Therefore

$$\begin{aligned} \frac{F'}{F} &= \frac{8.02 \times 10^{-5}}{2.60 \times 10^{-38}} \\ &= 3.08 \times 10^{33}, \end{aligned}$$

that is, the force of the area-enclosure about the molecules to cause their coalescence is inconceivably great in comparison with that of the attraction of their masses by gravitation.

Further, let two water molecules be at a distance x from centre to centre.

Then

$$F = G \frac{m^2}{x^2}.$$

Now the work performed in separating them farther by a small distance δx is $F \cdot \delta x$ or

$$G \frac{m^2}{x^2} \cdot dx,$$

and the whole work performed in separating them from contact to an infinite distance apart is

$$Gm^2 \int_d^\infty \frac{dx}{x^2} \text{ or } \frac{Gm^2}{d}.$$

If n is the number of molecules in a gram mass, the whole number of pairs of molecules is

$$\frac{n(n-1)}{2} \text{ or } \frac{n^2}{2}, \text{ approximately.}$$

The whole work, then, of separating the molecules to infinite distances apart

$$\begin{aligned} &= G \frac{m^2 n^2}{2d} \text{ or } \frac{G}{2d}, \text{ since } mn = 1 \\ &= .867. \end{aligned}$$

Thus the whole work of separating the molecules of a gram of water into its gaseous form against the Newtonian force of attraction is less than .867 ergs, or 6.46×10^{-8} calories. This is about 1.31×10^{-7} of its whole latent heat, and equal to about $\frac{1}{13}$ of the work required to separate a drop .6 cm. in diameter into three drops .5, .4, and .3 cm. in diameter.

We conclude, then, however reluctantly we may wish to do so, that the hypothesis of Laplace, which assumes that molecules attract each other, must be abandoned as having no physical justification. It is not capable of experimental proof. He conceived of it as an explanation of the phenomena of surface tension, but from the above considerations it fails to account for the coalescence of liquid drops and the condensation of a gas into its liquid condition.

We now see nature's law of transmission of energy. The heat of chemical combustion in the furnace is changed into potential energy of the area-forces about the free molecules into which the liquid water has been divided and separated. In this form the energy is carried from the furnace room to the radiators in the dwelling houses, or to the cylinders of engines, each molecule of steam carrying a load of 7.67×10^{-13} ergs. If the carrying pipes are properly "insulated" from outside influences, none or little of this potential energy is lost in transmission, the molecules being unable on account of their great velocities to coalesce and yield up their load. When the loaded molecules, however, reach the radiators,

which are constructed so as to be susceptible to these outside influences, by the exposure of a wide surface area to air at a much lower temperature, they coalesce very rapidly and yield up their load as they mass together in their liquid form. Then by radiation, convection, and conduction the temperature of the surrounding air and adjacent objects is raised by the addition of heat.

In the same way the heat radiated from the sun concentrates at the surface of the water surrounding the earth and forces the molecules through the area-force above the water mass into the air, each afterwards carrying its own definite load of potential energy. These water molecules with their loads become part of the movable gas envelope surrounding the earth and are carried with it to various parts of its solid surface. But for this the sun's energy would be radiated back into space almost as soon as received, in alternating quantities by day and by night, and life would be impossible on account of extremes of temperature. Thus the sun by multiplying the area-force enclosures loads the atmosphere with great quantities of molecular potential energy, which is again released by the coalescence of these enclosures, thereby raising the temperature of the air and objects on the earth's solid crust. These two processes are going on continually. If more enclosures are being formed than are coalescing, the temperature of the surrounding masses is thereby being lowered; but if less enclosures are being formed than are coalescing, the temperature of the surrounding masses is being raised. Thus the clouds, which are partly condensed water gas, are in a medium warmer than the air above; and as the mist further condenses into falling rain more heat is communicated to the layers of the air below. Moreover, the water thus brought to the earth's surface may again be made the vehicle to further transmit excess of energy from one part to another part where it is lacking.

Some idea of the enormous quantity of energy transmitted in this way may be gained by considering the yearly rain fall of 30 inches upon a garden plot 30 by 50 feet in the Niagara

peninsula. The energy supplied by the sun necessary to convert the water into molecular enclosures

$$= \frac{2.5 \times 40 \times 50 \times 1728 \times 495 J}{(.3937)^3} \text{ergs}$$

or 2.95×10^{20} ergs. If we consider this energy supplied by an engine, it would be required to work at a rate of

$$\frac{2.95 \times 10^{20} \times 1.34}{365 \times 24 \times 60 \times 60 \times 10^{10}}$$

or 1250 horse-power, night and day throughout the year, to furnish the water which is necessary for plant growth, and to supply the heat energy which is needed to modify the extremes of temperature.

It may be well to notice that the energy carried in this way into the cylinder of a steam engine is not available to do mechanical work. It cannot be converted by coalescence of the molecules into any other kind of energy than heat. It cannot be made to press the piston of the cylinder against outside resistance. In fact the opposite effect is produced, and work is done by the air pressure against the engine to the extent of 41 calories. Thus in a steam engine the heat of the furnace is available to do mechanical work after a fruitless expenditure of 536 calories. Every effort should be made to save this great waste.

But additional heat may be carried by the steam through the pipes as heat. This amount is $(\theta - 373)ms$, where θ is the absolute temperature, m is the mass, and s is the specific heat of steam. But here again, when the superheated steam is transmitted to the cylinders, the loss of heat on account of the high temperature by radiation, convection and conduction is very great. Of the total quantity of heat from the furnace only from 5 to 15 per cent. is used for the purpose intended.

Of the almost inconceivable quantity of energy received from the sun only an infinitesimal quantity is retained for a time in nature's store-houses upon the earth's surface. One of these store-houses is the water mass elevations of our inland lakes. The energy is available as the water falls to

lower levels by gravity and is continually renewed by the energy carried by the water molecules from the surface of the seas. But of this there is only a definite amount depending on the configuration of the earth's surface. There is not nearly enough to supply the dwellings of a civilized population in the temperate zones.

But nature has another store-house of almost unlimited capacity in the hydrocarbons of vegetable life. The heat and light of the sun in the presence of life, aided by the action of the molecular area-forces between unlike molecules, is constantly reversing the process of combustion. Out of its inexhaustible store the sun supplies the heat of chemical combustion of the hydrocarbons where it is held in compact space in great quantities. Of this there is no limit. But we in our destructive ignorance have already worked almost irremediable havoc with our supply. With axe and saw and fire we have stripped thousands of square miles of this heat energy and left no means whereby nature may restore it. The demand for space in printed paper for news, advertising, books, magazines, and statistics will soon strip the habitable world bare. The cost of growing a fir tree, which the lumberman cuts down without a thought, requires in one item alone enough energy to keep an engine of 500 horse-power running steadily for 150 or 200 years. A single issue of the *Ladies' Home Journal* costs the sun a power equal to that of Niagara Falls for a month.

The remedy is in our hands. For our own preservation we must search out the laws which govern this storage of energy, and through a better knowledge of them create conditions whereby nature may increase this store. Practically, we should study to find the woods which have the greatest calorific value, and see to it that for every tree that is cut down two shall be growing in its place. A better construction of our dwellings and more wool fibres in our clothing would help conserve our heat also.

There is more hope for our future supply of energy along this practical line than in the dream of releasing the energy stored up in the atom. The sun is already pouring it forth

in available profusion. It is within the power of man to control it. What we need is more knowledge of how nature works along her own lines by her own definite laws.

II

We have seen that by examining the loss of potential energy in the surfaces of two water drops when they coalesce we were led to consider the existence of an area-force about the free molecules of a gas; that the action of the area-force is quite distinct from that of the Newtonian attraction; that this force surrounds every free molecule of a gas, every free mist particle, every free solid particle, and every free aggregation of molecules; that it marks the boundary where the phenomena of matter are added to those of ether; that it becomes evident only when two free force enclosures come into contact; that in every case the force causes motion by changing the potential energy of the free areas of the enclosures into heat energy of the masses; and that, in fine, this area-force is the controlling force in all molecular action.

This view of the molecular world greatly simplifies our conception and explanation of many phenomena known by widely different names. By this view the molecules in a liquid preserve their identity, and, except under very extraordinary conditions, their volume also. They may slip by one another freely without friction and change their shape and their surface area greatly. One needs only to see a quantity of fish in a box to understand how a volume may be completely filled up by forms other than geometrical. We believe the water molecule is one which in its liquid condition may adapt its form so as to furnish a medium through which nature performs her processes of growth and change. It is in this change in form and in relative position, without change in volume, that the Brownian movement of the molecules, which is now generally identified with heat, consists. Thus any mechanical disturbance would increase this form-activity and raise the temperature. It would account completely for the discontinuous movements of spheroid particles suspended in liquid, which have been studied by Einstein and whose

formulae has been adopted by Perrin in his work on *Atoms*. Each of these investigators regarded the suspended spheroid as being knocked about by the much *smaller spheroids* of water. It may be that this is the cause of Perrin's value of N being so much larger than that determined by Jeans in his *Dynamical Theory of Gases*, and that by Millikan in his work on *The Electron*. These latter considered the motion of the spheroid in a gas where the molecules are spherical.

It is thus possible to visualize the escape of a molecule from its liquid. It cannot emerge unless energy is supplied to force it through the strong area-force about the mass itself. This energy must be precisely equal to the potential energy which the escaped molecule must afterwards carry. The manner of its escape is similar to that of a water drop being detached from the mass above by gravity as it falls from a dropper; only the action is immeasurably quicker and more vigorous in proportion to the mass ejected. But there can be no smaller molecules formed between as in the case of the water drop. Once the molecule is free there is no attraction to cause it to return to the surface again. It requires no energy to bring the molecule from the interior of the liquid to a position in contact with the surface about the mass. After contact the energy supplied will be proportional to the increase in area as the molecule is lifted above the liquid level.

Let the portion ACB of the molecule be forced above the level of the liquid a distance x (Fig. 1). Then the energy required to do this work

= the potential energy of the curved area ACB diminished by that of the plane area AEB .

$$= 2\pi r x \cdot T - \pi \cdot A E^{-2} \cdot T.$$

$$= 2\pi r x T - \pi T \{ r^2 - (r-x)^2 \}.$$

$$= \pi x^2 \cdot T$$

where x may not greatly exceed d . The distance x may be greater than d by reason of the force-neck that is formed just before the molecule breaks away. Thus the energy required to force a molecule partly out of its own liquid is

approximately proportional to the square of the distance of its upper rim from the liquid level. Since πx^2 is the area of a sphere whose diameter is x , this energy is equal to that of a hypothetical molecule whose diameter is the perpendicular distance the molecule is projected above the surface level. Thus the energy required to force it half way out is equal to $\pi r^2 \cdot T$, which is $\frac{1}{4}$ of the total amount required to force it all the way out; and therefore to force out the second half requires three times as much energy as to cause the first half to emerge. Or, again, half of the total energy of projection will force it $\frac{1}{\sqrt{2}}$ or .707 of its way out.

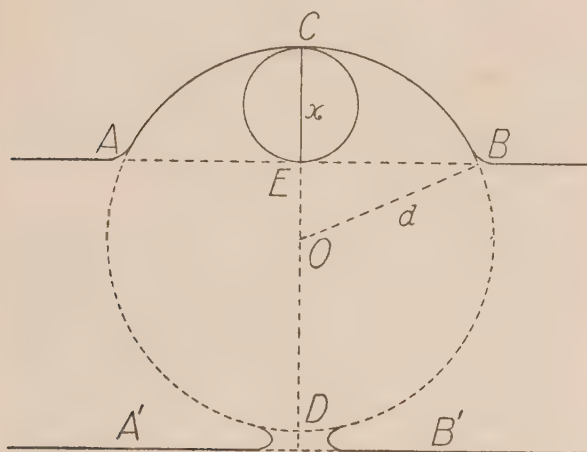


Figure 1

When the emergence is nearly complete so that the molecule is submerged by a small distance δd , the energy required to complete the ejection

$$= \pi T \cdot [(d^2 - (d - \delta d)^2)]$$

$$= 2\pi d \cdot \delta d \cdot T - \pi(\delta d)^2 \cdot T$$

$$= 2\pi d \cdot \delta d \cdot T \text{ very approximately.}$$

This is just twice the energy of the surface of a cylinder whose diameter is d and length δd . But we have seen that the energy required to lift the molecule above the surface level a small distance δd is $\pi T(\delta d)^2$. The ratio which the

former of these two amounts bears to the latter is $\frac{2d}{\delta d}$, a quantity approaching infinity. The sudden expenditure of this enormous amount of energy distributed over an infinitely small vanishing distance δd would call into play enormous forces just as the molecule leaves the surface, and the final ejection of the molecule would be difficult if not impossible. But nature provides a means of obviating this. For a short distance before the separation takes place (geometrically speaking) the force-areas are stretched out of their true shape and form a force-neck of an immaterial elastic nature which allows an increased distance of separation before all the energy is used up. Thus the violence of the last act of separation is greatly modified. Nevertheless, the final escape of the molecule is accomplished only because its next neighbour is in violent vibration against it. This is shown in Fig. 2, where the energy expended in forcing a molecule partly out of its liquid is plotted as ordinate against the distance its upper rim is above the level as abscissa.

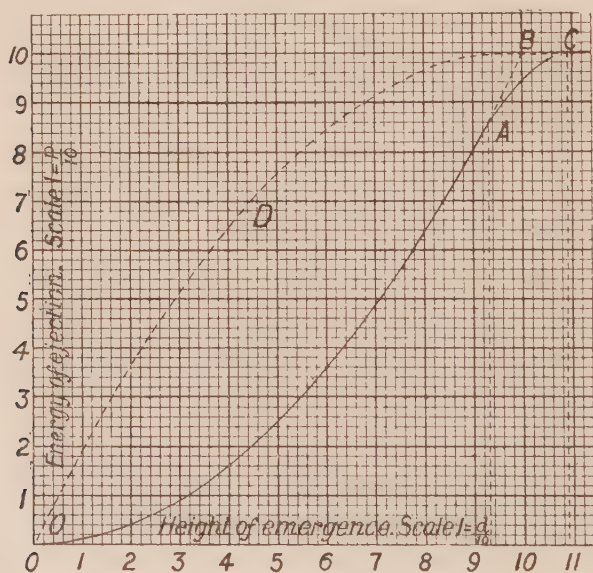


Figure 2

The portion OA of the curve, which is a true parabola, shows the law of the storage of potential energy in the force-area about the molecule until the force-neck begins to act. The portion AC shows the law AB as modified by the action of the force-neck.

In the same way we may trace the storage of potential energy in the surface of a water drop when it is caused to emerge through the force-area of the water mass.

This formula is more correct than that established by Laplace and others, who make the energy of ejecting a molecule from its liquid depend upon molecular attraction at and near the surface of the liquid. They consequently use the term $\frac{a}{v^2}$ where a is the mutual attraction of two molecules, and v is the volume of the mass which is subject to this attraction and consequently to the unequal pressure at the surface. There is, however, a marked divergence of opinion in regard to the quantity a . Some, as van der Waäls, treat it as a constant, while others, as Joule and Berthelot, treat it as an inverse function of θ . But it is a pure assumption that molecules either attract or repel each other, and, consequently, the formula

$$\left(p + \frac{a}{v^2}\right) (v - b) = R\theta$$

does not truly represent the law of gaseous pressure during the process of the change of a molecule from its liquid to its gaseous condition.

On the other hand, however, when a molecule or liquid drop approaches a free surface of its liquid, there is no action whatever until geometrical contact actually takes place. Then the change in potential energy begins abruptly as indicated by the sharp angle which the parabola makes with the horizontal at B . Thus is caused the sudden jerking of the molecule or liquid drop into the liquid.

This property which the free area-force enclosures have of uniting and forming an elastic force-neck is fundamental. Without it there could be no coalescence at all, nor could a

molecule be separated from the liquid mass within whose force-enclosure it happened to be. There is abundant evidence of it when we examine the action of visible liquid drops of all kinds, and we have reason to infer that the same is true in regard to molecules.

Further, if two drops of water strike together with sufficient relative velocity, they will at first unite their force-areas and for an instant one force-enclosure will envelop the whole mass; but, on account of the masses possessing large kinetic energies in addition to their potential energies, they are unable to convert this energy rapidly enough into heat, and the combined mass may be broken up into a number of smaller spheres having more potential surface energy, more heat, and less kinetic energy than before.

In the same way, if two spherical molecules collide with great relative velocity, they will remain united for a short time in one force-enclosure with less potential energy of their areas and more kinetic vibration energy of their masses. The total kinetic vibration will then be great enough to drive them apart again, and on account of their perfect elasticity their energies will be restored as they were before collision. There will, however, be a point where the kinetic energy of the separate molecules (heat) will not be sufficient along with the vibration energy produced by coalescence to cause the molecules to fly apart again. In this case coalescence will be permanent, that is, condensation will take place at a fixed temperature of the gas. There should thus be a connection between the amounts of the potential surface energy (E) and the kinetic vibration energy (H) of the individual molecules at the boiling points (θ) of the several liquids. Now E is a fixed quantity for all temperatures of a given gas, while H , which is a linear function of θ , differs with the different boiling points.

The quantities θ , E , and H have been calculated for sixteen substances for which the necessary experimental data are available. In Fig. 3 following, E has been plotted against H . The points (H , E) for twelve of these substances are seen to lie very approximately along a regular curve resembling

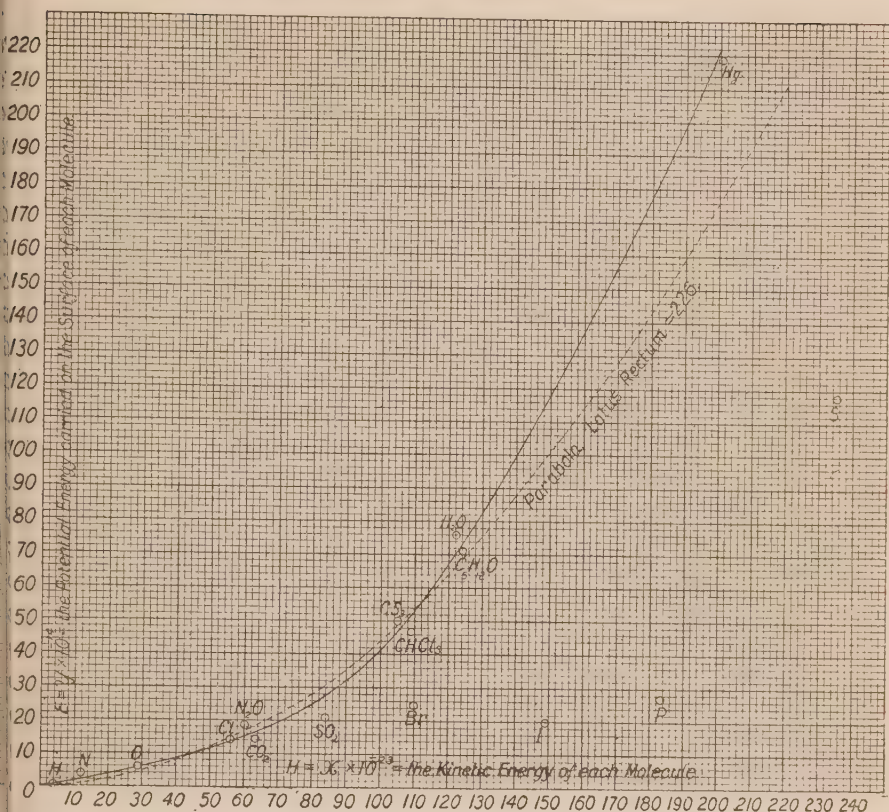


Figure 3

the half of a parabola whose vertex is at the point corresponding to 0° absolute. For the remaining four, as we may expect from the uncertain values of E , the points (H , E) are away from their true positions, and consequently do not group themselves with the others on the curve. Also, SO_2 is a little out of line for the same reason. The dotted curve is made to pass through the point for water.

If this curve represents even approximately the law connecting the potential surface energies of the free molecules with their kinetic (heat) energies at the boiling points, we

see that those substances which have high boiling points possess also high molecular potential energy. The latter depends on the diameter of the free molecule and the tension of its area-force. By far the greater part of the earth's crust is composed of substances whose boiling points are high, and consequently, when the earth was a mass in a gaseous condition, the potential energy carried by the free molecules was very great. This enormous potential energy was then gradually turned into heat by the coalescence of the molecules as they took their liquid form. The energy thus relieved would be sufficient to maintain the heat of an astronomical body for millions of years at a somewhat constant temperature; for the excess of the heat energy must be radiated into space until the coalescence of the free molecules is completed and the mass is a liquid.

After this point is reached the body will cool down to the temperature of solidification; and, when a somewhat similar period of stationary temperature has been passed through, the body by radiation will cool still further until, were it not to receive radiation of heat from countless other heavenly bodies, the cooling would proceed to absolute zero. The earth has passed through the first stage for those substances whose molecular potential energy is high. The gases helium, hydrogen, nitrogen, oxygen, and some compounds have low potential surface energy. It has nearly completed the second stage, water being almost the only exception.

The sun, however, is in the process of becoming a liquid, giving up great quantities of radiant energy while maintaining a constant temperature. Here, again, this enormous radiation from the sun keeps a somewhat equalized temperature upon the earth which but for this would soon lose all its heat. Thus the heavenly bodies maintain long periods of constant temperatures through the aeons of their existence.

ARTICLE VIII

THE DETERMINATION OF AVOGADRO'S NUMBER BY SURFACE TENSION PHENOMENA

The fact that all free liquid masses are of a spherical form, whether they are floating in a gas or suspended in another immiscible liquid, suggests to us that they are surrounded by something of the nature of an elastic envelope, which acts as though it were trying to compress the mass into a smaller volume by contracting its surface area to a minimum. The additional fact that, if two such spheres of the same liquid touch each other, they at once unite and form a single drop or sphere, whose surface area is less than that of the component spheres, suggests a means of arriving at some properties of matter that have not previously been considered. May not the free molecule be surrounded by such an elastic envelope? And may not free molecules unite their masses on contact just as free liquid spheres do? If so, much of the difficulty in our present knowledge of surface tension will be cleared up, and other questions of importance will be opened up for investigation from this new point of view.

Now the potential energy existing in the elastic envelope about a free water sphere is measured by the product of the measures of its area and its tension. There is, therefore, a decrease of potential energy in the envelopes about the two masses as they coalesce and take their new form. In doing this, work is done, *i.e.*, a definite part of the potential energy of the envelopes is transformed into heat.

Thus, three free water spheres whose diameters are .3, .4 and .5 cm. will unite to form a single sphere whose diameter is .6 cm. and whose surface area is $.14 \pi$ sq. cm. less than that of the component spheres. Taking the tension of the envelope at standard temperature, 15° C., to be 74.2 dynes per cm., we have a decrease of potential energy of the envelope amounting to 10.39π ergs, or, in heat units, to 7.80×10^{-7} calories.

Now the coalescence of water spheres takes place on

contact at all temperatures for which the water is liquid. If, therefore, a very large number of these spheres coalesce to form a given mass, the heat produced will be considerable.

Let n = the number of these water spheres in a gram molecule,

d = the diameter of each in cm.,

D = the diameter of the gram molecule sphere,

L = the latent heat of a gram mass of gaseous water in calories,

T = the tension of the envelope about each water sphere.

Equating the volumes before and after coalescence, we have

$$\frac{n\pi d^3}{6} = \frac{\pi D^3}{6}$$

from which $d = D \cdot n^{-\frac{1}{3}}$. Further, the potential energies of the envelopes before and after coalescence are $n\pi d^2 \cdot T$ and $\pi D^2 T$ respectively. The amount of potential energy of the envelopes which is converted into heat is, therefore, $\pi T(nd^2 - D^2)$, which by the relation above may be written $\pi TD^2(n^{\frac{2}{3}} - 1)$. Now, since n is very large in comparison with unity, $n^{\frac{2}{3}} - 1$ differs but little from $n^{\frac{2}{3}}$, and thus this amount is $\pi TD^2 \cdot n^{\frac{2}{3}}$. Now

$$\frac{\pi \cdot D^3}{6} = 18,$$

hence the potential energy transformed into heat when the n water spheres coalesce to form a gram molecule is $18(2\pi)^{\frac{1}{3}} T \cdot n^{\frac{1}{3}}$. The potential energy thus transformed into heat varies then as the cube root of the number of water spheres which obey the law of coalescence, provided T remains constant. This will be the case if the temperature remains constant, that is if the heat is transferred to other masses, such as the surrounding air and adjacent solids. If, then, there is no limit to the number of these water spheres, there is no limit to the quantity of heat produced by their coalescence.

But there is a limit, which is known as the latent heat of condensation, L , to the quantity of heat produced when a gram mass of water in its gaseous state is condensed into its

liquid state at the same temperature. We shall, therefore, have

$$18(2\pi)^{\frac{1}{3}}T \cdot n^{\frac{1}{3}} = 18 \cdot L \cdot J,$$

from which

$$n = \left(\frac{LJ}{T} \right)^3 \times \frac{1}{2\pi}.$$

Now, for all temperatures of water above 4° C. to 365° C. (about 40° C. below the critical temperature) it has been shown experimentally that the surface tension T about large masses is a linear function of the absolute temperature. This result is expressed in the empirical formula $T_{\theta} = A + B\theta$, where A and B are constants. It has also been shown (see Kaye and Laby's tables for authorities) that when $\theta = 638^{\circ} \text{ A.}$, $T = 0$; and that when $\theta = 288^{\circ} \text{ A.}$, $T = 74.2$. We have, therefore

$$T_{\theta} = 135 - .212 \theta,$$

whence

$$T_0 = 135.$$

It is evident that only in large spheres can the tension of the envelope obey the law given above, for only in these can the heat motion of the molecules next the envelope affect the tension. For spheres containing only a few molecules and for the free molecules themselves the heat motion is the motion of the sphere itself. The tension, therefore, of the envelope about the free molecule will be very approximately that of a large sphere when the molecules are at rest, that is, when the temperature is 0° A.

If this law held throughout the process of solidification, would the tension of the envelope about the free water molecule be 135? During solidification the sphere suffers a decrease in density which at 273° A. is .9164; and consequently its envelope is expanded in the ratio of (.9164)³ to 1. Now the process of solidification depends upon forces in the interior of the molecule. The surface energy of the mass, which does not depend on these forces, therefore remains unchanged during the process. Thus, the tension of the envelope about the solid sphere per unit of length is

$(.9164)^{\frac{2}{3}}$ of its value about the liquid sphere. This appears to be a reasonable conclusion when we consider that the envelope in expanding does not cause any change in the number of molecules on the surface but only, as it were, increases the space allotted to each next the envelope.

Again, as the temperature changes from 373° A. to 0° A. there is a change in density which, for the same reason as before, would cause a change in the tension. But of this we have no data. However, we may without serious error assume that these two opposite causes counteract each other; for the density at 0° A. where the molecules are at rest would not differ materially from the maximum density at 277° A., at which point the decrease in the density began in the process of solidification.

If we denote the final density at 0° A. by ρ , the absolute tension of the envelope T_m would be $\rho^{\frac{2}{3}} \times 135$ where ρ does not differ much from 1. Hence

$$n = \left(\frac{L.J}{T_o} \right)^3 \times \frac{1}{2\pi\rho^2}.$$

If we take $T_o = 135$, $L = 498$ (which is the heat equivalent of internal work for steam at 100° C.) $J = 4.184 \times 10^7$ and assume that $\rho = 1$ we have by calculation, $n = 5.85 \times 10^{23}$. Millikan's value for this number obtained by his "balanced drop method" is 6.065×10^{23} , while Perrin's value obtained by observing the motion of a colloidal sphere in water is 6.67×10^{23} .

The above result furnishes an argument in favour of the view that the free molecule does possess something of the nature of an elastic envelope about it; that, in fact, it possesses a strong surface tension of the same nature as that about a visible water sphere. Hence also it carries its own definite quantity of surface energy which is quite independent of its kinetic energy or heat.

If this be so, it goes to show that the properties of surface tension can be considered as not depending upon the "mutual attraction of molecules." For, if the free molecule

has about it this elastic envelope, it is plain that the envelope cannot be a material thing at all. It is simply a force and nothing more.

Now, since the force of gravity in its relation to potential energy is denoted by $\frac{dE}{da}$, this force will be denoted by $\frac{dE}{dA}$,

where E is potential energy, a is length, and A is area. Also because of its elastic nature this envelope tends to compress the interior of the sphere into a smaller volume, but is prevented from doing so by a force in the interior which must therefore be denoted by $\frac{dE}{dV}$ where V is volume. It may be

that all physical phenomena may be expressed in terms of these three fundamental physical forces, of which, beyond these distinguishing characteristics, we know but little.

Thus we see why the ordinary formulae of surface tension break down for surfaces of small masses; for they embody the experimental results obtained when only a portion of the force envelope about a large mass is considered. The investigations of Rücker and Reinold in 1886 and many others since show that the surface tension of thin liquid films is subject to abrupt changes for thicknesses of the films even larger than 12×10^{-7} , or 30 times the diameter of the molecule. The writer believes, however, from experimental evidence which has come into his possession and which he has prepared in a separate article, that this phenomenon may be consistently explained from the point of view expressed above.

But the formula obtained above appears to hold for all masses whatever be their size. For, since it gives a value of N practically identical with those we already know, it suggests that the law of coalescence of water spheres does not break down at any point, from the coalescence of large spheres to the coalescence of small spheres down to molecules themselves. The method of obtaining the formula embodies in its essence discontinuity of action, involving from the beginning to the

end no less than p distinct acts of coalescence, where $2^p = \frac{N}{18}$, so that $p = 75$.

At first thought it would seem that in the latter stages of the condensation, where large spheres coalesce, the decrease in T on account of the heat motion would greatly modify our value of N . Whatever effect this would have, however, would only tend to increase the value. But the increase must necessarily be very slight. For, suppose the first act of coalescence was to form the molecules into pairs, so that the resulting spheres each contain two molecules. Then, if we consider only a gram mass, the first act of coalescence may be proved to cause a decrease of potential energy amounting to $L(1-2^{-\frac{1}{2}})$ calories; the second act a decrease of $L(1-2^{-\frac{1}{2}}) \times 2^{-\frac{1}{2}}$ calories; the third act a decrease of $L(1-2^{-\frac{1}{2}}) (2^{-\frac{1}{2}})^2$ calories; and so on, the q th act causing a decrease of $L(1-2^{-\frac{1}{2}}) (2^{-\frac{1}{2}})^{q-1}$ calories. These results are given in the table below.

TABLE I

The q th order	Decrease for the q th act
1	102.6 calories
2	81.4 calories
3	64.6 calories
4	51.2 calories
5	40.7 calories
.....
21	1.0 calories
.....
75 (final)	.00000385 calories

At the end of the fifth act the spheres consist of 32 molecules, but the gram mass has suffered a total decrease of 340.5 calories of potential energy, or of 68 per cent. After the 21st act, which causes a decrease of only 1 calorie, the total surface energy remaining is 3.91 calories, or considerably less than 1 per cent. Thus the change in T on account of heat motion in the large spheres towards the latter part of

the process of condensation does not affect the value of N materially. Thus also the measured value of T causes the calculated value of N to be widely divergent from the true value, even as much as 6.02 times too great.

Since the formula obtained above is independent of the molecular weight m and gives the value of N so accurately from data experimentally determined in connection with water, the idea is suggested that it would also give the same value from similar data in connection with any other chemically stable substance such as methyl alcohol. But when we search for these data we find few are available. With some substances one or more are lacking, while with others the determinations recorded are by only one method and lack corroboration.

For ethyl alcohol, however, we have:

$\theta_c = 518^\circ \text{ A.}$, determined by Ramsay and Young in 1886,

$T_\theta = 22$ at 288° A. , by Ramsay and Shields in 1893,

$L = 186.8$, by interpolation of values determined by Young in 1910 and corrected for external work. It is well to observe that 288° A. is 127° above the melting point at 161° A. and 63° below the boiling point at 352° A. , and that there are no other reliable determinations for T_θ through a range of temperature of 357° from the melting point to the critical temperature 518° A.

Hence, assuming that the law $T_\theta = A + B\theta$ holds for alcohol and using the data above we find that

$$T_\theta = 49.5 - .0965 \theta,$$

from which

$$T_o = 49.5.$$

Then the formula gives by calculation $N = 3.15 \times 10^{23}$, a value a little more than one half the true value. If, however, we had used $T = 17.9$ instead of 22, and consequently $T_o = 40.5$ instead of 49.5, we should have obtained the true value. These predicted values are within an accumulated experimental error of 18 per cent. There seems, then, no reasonable doubt that, if we knew more accurately the temperature changes in T_θ , we should find the molecular surface tension

to be about 17.9, that is, provided the other determinations are correct.

These results seem to confirm the conclusion that the formula

$$N = \left(\frac{dJ}{T_m} \right)^3 \times \frac{1}{2\pi}$$

is true for all chemically stable substances, that is, it represents a universal relation among the quantities involved for such substances. If this be so, then

$$\frac{T_m}{L} = \frac{J}{(2\pi N)^{\frac{1}{3}}}$$

that is, the molecular surface tension of a free molecule of any gas bears a constant ratio to the latent heat of a gram mass of the gas. This constant ratio is $\frac{J}{(2\pi N)^{\frac{1}{3}}}$, or .271; and since this ratio is independent of the diameter and density of the free molecule, T_m , which we have denoted by $\frac{dE}{dA}$, is not a property of mass but is a property of matter, that is, it changes only for different kinds of substances. On the other hand gravity, or $\frac{dE}{da}$, is not a property of matter but is a property of mass, being independent of the kind of substances.

Again, if d be the diameter and m be the molecular weight of the free molecule and E_m and T_m be its surface energy and tension, we shall have

$$E_m = T_m \times \pi d^2,$$

or

$$\frac{L \cdot J \cdot m}{N} = \frac{LJ}{(2\pi N)^{\frac{1}{3}}} \times \pi d^2,$$

from which

$$d = \frac{(2m)^{\frac{1}{3}}}{(2\pi N)^{\frac{1}{3}}} = \frac{6}{(2\pi N)^{\frac{1}{3}}} \text{ for the free water molecule.}$$

Again, consider the space allotted to a molecule of water in its liquid state at 4° C. when $\rho = 1$. If d' be the spherical

diameter of this space, we have

$$\frac{\pi d_1^3}{6} = \frac{18}{N},$$

whence

$$d_1 = \frac{6}{(2\pi N)^{\frac{1}{3}}} = 3.89 \times 10^{-8}.$$

Thus $d = d_1$. That is, the volume of the free water molecule is exactly equal to the space it occupies in the liquid at maximum density. At 100° C. , however, the density of water is .9584, so that, if d_2 be the diameter of the space it occupies in water at the boiling point, we have as before

$$d_2 = \frac{6}{(2\pi N)^{\frac{1}{3}}} \times \frac{1}{\rho^{\frac{1}{3}}} = 3.94 \times 10^{-8}.$$

This would allow a lateral space for heat vibrations amounting on the average to the difference of these diameters, which is 5×10^{-10} , or about 1.3 per cent. of the diameter of the molecule.

For alcohol, however,

$$d = \frac{(2 \times 46)^{\frac{1}{3}}}{(2\pi N)^{\frac{1}{3}}} = 6.22 \times 10^{-8}.$$

As we do not know any limit to the density of alcohol, as in the case of water, we have no means of comparing the space occupied in its free state and that at the limit of density in the liquid state. At 15° C. $\rho = .7937$ at which point the coefficient of its expansion is .00110 and increases with increase in temperature. At the boiling point, 78° C. , if $\rho = .624$,

$$d_1 = \left(\frac{6 \times 46}{\pi \rho N} \right)^{\frac{1}{3}} = 6.22 \times 10^{-8},$$

so that $d = d_1$.

It is quite reasonable to suppose that at the boiling point the density is considerably less than .624, in which case d_1 would be larger than d and there would be space for heat vibrations of the molecules as there is in liquid water. There is, however, a difficulty, for the space allotted to the molecule in the liquid at 15° C. has a spherical diameter of only 5.74×10^{-8} and it would seem that in some way the molecules

in the liquid individually take up less space than they do when free. They must have a diameter in the liquid even less than 5.74×10^{-8} so as to allow for heat vibrations. The explanation may lie in the atomic structure of the molecule.

Again, for the free molecule of all substances we have

$$d = \frac{(2m)^{\frac{1}{2}}}{(2\pi N)^{\frac{1}{2}}},$$

or

$$d = \frac{2^{\frac{1}{2}}}{(2\pi N)^{\frac{1}{2}}} \times m^{\frac{1}{2}},$$

that is, the diameter of the free molecule is proportional to the square root of its molecular weight. Also, if s be the surface area of the molecule, so that

$$d = \left(\frac{s}{\pi} \right)^{\frac{1}{2}},$$

then it follows that

$$s = \left(\frac{2\pi}{N^2} \right)^{\frac{1}{2}} \times m,$$

and the surface area of the molecule is directly proportional to its molecular or atomic weight.

We are thus led to the conception that, regardless of the size of the free molecule, each element of the atomic mass occupies or controls a definite space on the free molecular or atomic surface. Thus, if a denotes this area, we have

$$\begin{aligned} a = \frac{\pi}{m} d^2 &= \frac{\pi}{m} \frac{2m}{(2\pi N)^{\frac{1}{2}}} = \frac{2\pi}{(2\pi N)^{\frac{1}{2}}} \\ &= 2.64 \times 10^{-16}, \text{ a definite physical constant.} \end{aligned}$$

Nor does there seem any alternative to the idea that these elements of atomic mass can be in equilibrium only when they are symmetrically arranged on the surface. This suggests the idea that in the free atom the structure depends upon the arrangement of the elements of the atomic mass in equal unchangeable areas on the surface of the atom, and also that the stability of the free atom depends to some extent upon the difficulty which this element of atomic mass has in wrenching itself, as it were, out of the force area about the atom.

NOTE.—(1) If $T_{288} = 71.4$, which was determined by

Ramsay and Shields in 1883 as the tension between water and its vapour, we have

$$T_o = 130, \text{ and } N = 6.56 \times 10^{23}.$$

(2) If ρ_θ denote the density of water at $\theta^\circ \text{ A.}$,
 then, if $\rho_o = .892$, $N = 6.065 \times 10^{23}$,
 if $\rho_o = 1.000$, $N = 5.85 \times 10^{23}$,
 and if $\rho_o = .9365$, $N = 6.67 \times 10^{23}$.
 Also, for ice at 0° C. $\rho = .9164$.

(3) There is no doubt that in the liquid when the surface tension is measured the rate of passage of molecules through the force envelope either way will modify the formula $T_\theta = A + B\theta$. Now this rate of passage of the molecules changes with the temperature and is therefore a function of θ . We shall thus have

$$T_\theta = A + B\theta + f(\theta)$$

where the effect of $f(\theta)$ upon T_θ is small.

The investigation into the exact nature of these corrections for the value of T_o , though it may be difficult, should prove interesting.

TABLE OF ATOMIC DIAMETERS

We have

$$d = \frac{(2m)^{\frac{1}{3}}}{(2\pi N)^{\frac{1}{3}}},$$

the diameter of the free molecule, and

$$d_1 = \left(\frac{6m}{\rho\pi N} \right)^{\frac{1}{3}},$$

the spherical space occupied by the molecule in the liquid or the solid whose density is ρ at some convenient temperature.

Name	Symbol	m	$d \times 10^8$	ρ	$d_1 \times 10^8$
Hydrogen.....	H	1	.9165	.068 (solid)	3.44
				.07 (liquid)	3.60
Helium.....	He	3.99	1.832	.15 (liquid)	4.43
Lithium.....	Li	6.94	2.41	.534	3.49
Beryllium.....	Be	9.1	2.76	1.93	2.50
Barium.....	B	11.0	3.04	3.75	2.12
Carbon.....	C	12.0	3.17	3.52 (diamond)	2.23
				2.3 (graphite)	2.55
Nitrogen.....	N	14.01	3.43	.79 (liquid)	3.87

TABLE OF ATOMIC DIAMETERS—*Continued*

Name	Symbol	<i>m</i>	$d \times 10^8$	ρ	$d_1 \times 10^8$
Oxygen.....	O	16.0	3.67	1.27 (liquid)	2.74
Fluorine.....	F	19.0	3.99	1.11 (liquid)	3.82
Neon.....	Ne	20.2	4.12	?	
Sodium.....	NA	23.0	4.39	.971	4.26
Magnesium.....	Mg	24.32	4.52	1.74	3.57
Aluminium.....	Al	27.1	4.77	2.65	3.22
Silicon.....	Si	28.3	4.88	2.3	3.42
Phosphorus.....	P	31.04	5.11	2.20 (red)	3.60
				1.83 (yellow)	3.83
Sulphur.....	S	32.07	5.19	2.07	3.70
				1.81 (liquid)	3.87
Chlorine.....	Cl	35.46	5.45	2.49 (liquid)	3.46
Potassium.....	K	39.1	5.73	.862	5.29
Argon.....	A	39.88	5.79	1.4 (liquid)	4.53
Calcium.....	Ca	40.09	5.80	1.55	4.39
Scandium.....	Sc	44.1	6.08	?	
Titanium.....	Ti	48.1	6.35	3.34	3.54
Vanadium.....	V	51.06	6.55	5.5	3.10
Chromium.....	Cr	52.0	6.61	6.50	2.97
Manganese.....	Mn	54.93	6.79	7.39	2.90
Iron.....	Fe	55.85	6.85	7.81 (pure)	2.85
Nickel.....	Ni	58.68	7.02	8.9	2.79
Cobalt.....	Co	58.97	7.04	8.6	2.82
Copper.....	Cu	63.57	7.31	8.93	2.85
Zinc.....	Zn	65.37	7.41	7.1	3.04
Gallium.....	Ga	69.9	7.66	5.95	3.37
Germanium.....	Ge	72.5	7.80	5.47	3.51
Arsenic.....	As	74.96	7.94	5.73	3.50
Selenium.....	Se	79.2	8.06	4.5 (crystal)	3.86
				4.27 (liquid)	3.93
Bromine.....	Br	79.92	8.19	3.102	4.73
Krypton.....	Kr	82.9	8.34	2.16 (liquid)	5.00
Rubidium.....	Rb	85.45	8.47	1.532	5.67
Strontium.....	Sr	87.63	8.58	2.54	4.72
Yttrium.....	Y	89.0	8.64	3.8 (?)	4.11
Zirconium.....	Zr	90.6	8.72	4.15	4.15
Niobium.....	Nb	93.5	8.87	12.75	2.47
Molybdenum...	Mo	96.0	8.98	8.6	3.32
Ruthenium.....	Ru	101.7	9.24	12.3	3.00
Rhodium.....	Rh	102.9	9.30	12.44	2.80
Palladium.....	Pd	106.7	9.47	11.4	3.13

TABLE OF ATOMIC DIAMETERS—*Continued*

Name	Symbol	m	$d \times 10^8$	ρ	$d_1 \times 10^8$
Silver.....	Ag	107.88	9.52	10.5	3.22
Cadmium.....	Cd	112.4	9.72	8.64	3.49
Indium.....	In	114.8	9.82	7.12	3.75
Tin.....	Sn	119.0	10.00	7.29	3.76
Antimony.....	Sb	120.2	10.05	6.62	3.90
Iodine.....	I	126.92	10.33	4.95	4.38
Tellurium.....	Te	127.5	10.35	6.25	4.05
Xenon.....	Xe	130.2	10.46	3.5 (liquid)	4.95
Caesium.....	Cs	132.81	10.57	1.87	6.29
Barium.....	Ba	137.37	10.71	3.75	4.93
Lanthanum....	La	139.0	10.81	6.12	4.20
Cerium.....	Ce	140.25	10.85	6.68	4.09
Praesodymium..	Pr	140.6	10.87	6.48	4.14
Neodymium....	Nd	144.3	11.01	6.96	4.07
Samarium.....	Sa	150.4	11.24	7.8	3.98
Europium.....	Eu	152.0	11.30		
Gadolinium....	Gd	157.3	11.51	(?)	
Terbium.....	Tb	159.2	11.56	(?)	
Dysprosium....	Dy	162.5	11.68		
Erbium.....	Er	167.4	11.86	4.77 (?)	4.96
Thulium.....	Tm	168.5	11.91		
Ytterbium.....	Yb	172.0	12.02	(?)	
Lutecium.....	Lu	174.0	12.09		
Tantalum.....	Ta	181.0	12.36	16.6	3.29
Tungsten.....	W	184.0	12.43	18.0	3.22
Osmium.....	Os	190.9	12.69	22.5	3.05
Iridium.....	Ir	193.1	12.73	22.41	3.04
Platinum.....	Pt	195.2	12.80	21.50	3.10
Gold.....	Au	197.2	12.87	19.32	3.22
Mercury.....	Hg	200.0	12.96	13.56	3.64
Thallium.....	Th	204.0	13.09	11.9	3.82
Lead.....	Pb	207.1	13.19	11.37	3.35
Bismuth.....	Bi	208.0	13.22	9.80	4.11
Radium.....	Ra	226.4	13.79	(?)	
Thorium.....	Th	232.0	13.96	11.3	4.06
Uranium.....	U	238.5	14.15	18.7	3.47

ARTICLE IX

THE STRUCTURE AND DISINTEGRATION OF LIQUID FILMS¹

I. INTRODUCTION

The stratified structure of liquid films, and especially those composing the soap bubble, was first established by Perrin² in 1918, and has been confirmed since by other investigators. He speaks, however, of this structure as enigmatic (*structure énigmatique*) and makes no attempt to explain it. More recently Wells³ in 1921 made an attempt to account for the structure on the basis of Langmuir's theory of atomic stability.⁴ But he has to admit that stratification is not at all necessary and only happens in preference to the spherical structure; and his explanation of this preference is rather complicated. The present paper is an attempt to throw some more light on the problem.

II. MOLECULAR FORCES

The Behaviour of Molecules. In May 1919, quite by accident, the writer was led to study the coalescence of free liquid spheres, and the main features of this investigation were published⁵ in June 1921. Briefly they are as follows:

The potential surface energy changed into heat by the natural coalescence of n liquid spheres of diameter d was found to be

$$\left(\frac{36m^2\pi}{\rho_o^2} \right)^{\frac{1}{3}} T_o n^{\frac{1}{3}},$$

¹This paper, translated into French, appeared in *Annales de Physique*, January-February, 1924. The editor, M. Marcel Brillouin, appended some notes which are given at the end.

²La Stratification des Lames Liquides, *Ann. de Phys.*, t. X, p. 160, 1918.

³L'épaisseur des Lames Stratifiées, *Ann. de Phys.*, t. XVI, p. 69, 1921.

⁴Fundamental Properties of Liquids and Solids, *Journ. Am. Chem. Soc.*, Vol. XXXIX, p. 1848, 1917.

⁵Coalescence of Liquid Spheres—Molecular Diameters, *Phil. Mag.*, Vol. XLI, p. 877, 1921.

where the mass considered was a gram molecule, and ρ_0 and T_0 refer to the density and surface tension at absolute zero. In seeking to account for this heat it was put equal to the latent heat of condensation of the gas, when the resulting equation for water gave a value of n equal to 6.15×10^{23} , with indications that the number should be slightly larger. This value agrees with those found by Perrin and Millikan for Avogadro's constant by methods of an altogether different nature. The significance of this unexpected result at once became evident.⁶ It indicated that the molecules of a gas in the first stage of condensation behave precisely as liquid spheres of visible dimensions do when they come into contact with each other, that is, they coalesce by being drawn into one sphere through the enveloping action of some force in their surfaces of the same nature as surface tension in larger masses.

The Nature of Molecular Forces. It follows, then, of necessity, that the free molecule of a gas possesses a force acting about its exterior surface in the same way as the surface tension force acts about a free liquid sphere. It further follows that this force, being active, or performing its function, in the area bounding molecular mass and ether-space, is fundamental in its nature. Like gravity, it can only be inferred by its visible effect on masses, and cannot, as yet, be expressed in terms of simpler elements. Thus, gravity acts to lessen the linear distance between the centres of two masses; this force acts to lessen the geometrical surface about a free mass. Surface tension, then, is an ether-mass phenomenon universally present in all free mass surface. It is entirely absent in the interior of a mass of a chemically pure liquid. Extended observations on the act of coalescence of liquid spheres shows that the process may be embodied in the following statement or law:

Whenever two free masses of the same liquid come into contact, their surface forces unite at the periphery of the contact area, and cease to act within the contact area itself.

⁶This result was not unexpected by the old physicists; see note at the end of this paper.—(Note by M. Brillouin).

In accordance with the preceding conclusions the law will be regarded as effective for molecular masses.

Molecular Forces in Emulsions. Again, observations on spheres of unlike liquids when brought into contact show that, as in the case of like liquids, coalescence always takes place. If the liquids are immiscible, as oil and water, one of the liquids envelops the other by forming a *uniform, closed, concentric shell or envelope* about it. If the liquids are miscible, in many cases the same action first takes place, and afterwards diffusion causes the liquid masses to intermingle. The law of action appears to be the same as before except that the force does not altogether cease to act in the contact area, but has a much weaker effect than in the free surface of either liquid.

It would appear in this way that the force is of the same nature as that which envelops the suspended spheres when one pure liquid forms a temporary emulsion with another pure liquid—temporary, because such free liquid spheres will coalesce whenever they come into contact. The permanency of such an emulsion is secured by the introduction of a small quantity of a suitable third liquid which throws a thin film of itself about the emulsion-forms, and thus prevents them from making contact with each other.

A Soap Solution is an Emulsion. Now, it happened, fortunately, while the writer was examining the contact of two spheres—the one of coal oil and the other of a soap solution used in the laboratory for class demonstration—that he found the soap solution to be an emulsion of the nature described above. It consisted of microscopic emulsion-forms closely arranged together. Evidently, the surface force about these forms was weak; for, on the surface of the solution they appeared as discs or lenses touching and overlapping one another while deeper in the liquid they were spheres. They were probably composed of glycerine surrounded by thin sheaths of oleate of soda and were separated from one another by water masses.

Observation of Movements. Without making any attempt to measure the thickness or the strength of the film, the

observations were directed to the movements and the processes by which the black-spot area was developed, the successive strata removed, and the bubble finally disrupted. A film with a slight convex curvature was formed over the top of a small cylindrical cup which was placed for protection in a closed vessel whose cover consisted of two glass plates inclined at an angle (Fig. 1). The light from a bright portion of the sky passed through one of the plates, was reflected by the film, and reached the eye after passing through the other plate. By means of a microscope adjusted at a proper angle from a movable support on the table the movements were seen in minute detail.

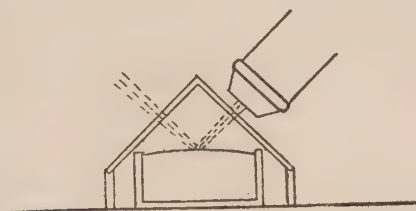


Figure 1.—Method of observing movements.

The Cause of the Stratification in the Soap Bubble. When the film was first formed a few emulsion forms, not greatly extended, were seen moving on the surface. Afterwards others more widely stretched out appeared to have their outer borders attached to the sides of the vessel. These evidently composed the elements of the stratified structure. They were in continual motion, adjusting themselves under the action of gravity, which tended to pull the water between the discs or strata downwards from the crest of the bubble, and the action of the surface forces which tended to diminish the potential surface energy. This latter process will be described in detail later on. It will assist in understanding these motions if one will conceive of a simple liquid film as composed of a mass of frictionless molecules having constant volumes but adjustable shapes, and as bounded on opposite sides by parallel surface forces, and *not as a thin mass of*

molecules attracting each other by centrally directed forces. For observing the whole process the writer found that a solution of pure castile soap in rain water gave admirable service.

III. THEORY OF DISINTEGRATION

It soon became evident, however, that these complex phenomena could be understood only by studying first the action of a film consisting of a single stratum. Premising, then, that such a film is of the nature described in the preceding paragraph it will be well to consider mathematically the following ideal proposition:

Under external and internal static conditions and independently of any gravitational, electrical, magnetic, or other centrally directed forces, a free uniform liquid cylinder of infinite length, or a free uniform plane liquid lamina of infinite extent, will, under the sole action of the surface forces bounding its mass, be in unstable equilibrium; and will under the slightest exterior disturbance immediately transform itself into spheres.⁷

Liquid Cylinders. Consider a length a of the cylinder whose diameter is d to be gathered into a sphere of diameter D . Then, by the equation of volumes, we have

$$\frac{\pi}{6} D^3 = \frac{\pi}{4} d^2 a,$$

whence

$$D = \left(\frac{3}{2} ad^2 \right)^{\frac{1}{3}}.$$

Again, the decrease in the potential surface energy

$$= T \cdot \pi da - T \cdot \pi D^2,$$

which, by the above relation, reduces to

$$T\pi ad \left(1 - \left(\frac{9d}{4a} \right)^{\frac{1}{3}} \right).$$

⁷This instability was studied in a complete manner by Plateau (*Statique expérimentale des liquides*, Vol. 2, ch. IX, X, XI. Especially pp. 207, 209. Gauthier-Villars, Paris, 1873. See Poincaré, *Capillarité*, ch. IV, p. 85. The experiments of Plateau, especially pp. 95 to 118. Carré, Paris 1895.— (Note by M. Brillouin).

If there is no change in the potential surface energy, we have

$$\frac{9d}{4a} = 1,$$

and, consequently,

$$a = \frac{9}{4}d,$$

and

$$D = \frac{3}{2}d.$$

For greater convenience, let us take a or $9d/4$ as unit of length and the potential surface energy of this length or of this sphere as unit of energy; then every other length which can be gathered into a sphere can be represented by ma or simply by m . If D_1 is the diameter of this sphere we have, as previously,

$$D_1 = \left(\frac{3}{2} mad^2 \right)^{\frac{1}{3}},$$

and the decrease in potential surface energy

$$= Tm\pi ad \left[1 - \left(\frac{9}{4} \frac{d}{ma} \right)^{\frac{1}{3}} \right],$$

that is to say, the decrease in energy for m units of length

$$= m \left[1 - \left(\frac{1}{m} \right)^{\frac{1}{3}} \right] \text{ units of energy.}$$

Then the decrease in energy per unit of length of the cylinder when the mass of m units of length is gathered into a sphere

$$= 1 - m^{-\frac{1}{3}} \text{ units of energy.}$$

If we denote by y this loss in potential surface energy we have

$$y = 1 - m^{-\frac{1}{3}}.$$

Now, since y is positive, zero, or negative according as m is greater than, equal to, or less than 1, no length of cylinder less than $9/4$ of its diameter can be gathered into a sphere without the addition of external energy. But the lengths greater than $9/4$ of the diameter will be gathered into spheres,

since in the process potential surface energy will be given up, that is, changed into heat, and there will be a tendency to increase without limit the length gathered into one sphere.

Liquid Laminae. Secondly, if the thickness of the lamina be d , and we consider a portion of it in the form of a regular hexagon whose diagonal is a to be gathered into a sphere whose diameter is D , we shall have as before on equating the volumes,

$$\frac{\pi}{6}D^3 = \left(\frac{3^{\frac{1}{2}}}{2}\right)^3 a^2 d,$$

whence

$$D = \frac{3^{\frac{1}{2}}}{2} \left(\frac{6a^2 d}{\pi}\right)^{\frac{1}{3}};$$

and the decrease in potential surface energy will be

$$2T \left(\frac{3^{\frac{1}{2}}}{2}\right)^3 a^2 - T\pi D^2,$$

which by the relation above reduces to

$$T \frac{3^{\frac{3}{2}}}{4} a^2 \left(1 - \left(\frac{4 \cdot 3^{\frac{1}{2}} \cdot \pi d^2}{a^2}\right)^{\frac{1}{3}}\right).$$

If there is no change in potential surface energy,

$$\frac{4 \cdot 3^{\frac{1}{2}} \cdot \pi d^2}{a^2} = 1,$$

and, consequently,

$$a = 2(\pi \cdot 3^{\frac{1}{2}})^{\frac{1}{2}} \cdot d,$$

and

$$D = 3d.$$

For convenience let one face of this hexagonal area, which is $\left(\frac{3^{\frac{1}{2}}}{2}\right)^3 a^2$ or $\frac{9}{2} \pi d^2$, be taken as the unit of area; then, any other hexagonal area may be represented by m^2 where its diagonal is ma . Also let the potential surface energy of the two hexagonal faces, or of the sphere, which is

$$T \cdot \frac{3^{\frac{3}{2}}}{4} \cdot a^2$$

be the unit of energy. Then, if D_1 be the diameter of the sphere into which this hexagonal mass is gathered, we shall have as before

$$D_1 = \frac{3^{\frac{1}{2}}}{2} \left(\frac{6m^2 a^2 d}{\pi} \right)^{\frac{1}{3}};$$

and the decrease in potential surface energy for m^2 units of area will be $m^2(1-m^{-\frac{2}{3}})$ units of energy. Therefore the decrease in potential surface energy per unit of area when m^2 units of area are gathered into one sphere is $1-m^{-\frac{2}{3}}$ units of energy. If y denotes this decrease we have

$$y = 1 - m^{-\frac{2}{3}}$$

Now, since y is positive, zero, or negative according as m is greater than, equal to, or less than 1, no hexagonal area of the lamina whose diagonal is less than $2(\pi \cdot 3^{\frac{1}{2}})^{\frac{1}{2}}$, or 5.075 times its thickness can be gathered into a sphere without the addition of external energy. But larger hexagonal areas than this will be gathered into separate spheres, since in the process potential surface energy will be changed into heat, and there will be a tendency to increase without limit the area gathered into one sphere.

In the table below are shown the changes that take place in potential surface energy per unit of length, or of area, when different cylindrical, or hexagonal, masses are gathered into spheres.

TABLE I

m	$1-m^{-\frac{1}{3}}$	$1-m^{-\frac{2}{3}}$	m	$1-m^{-\frac{1}{3}}$	$y=1-m^{-\frac{2}{3}}$
<1	<0	<0			
1	0.000	0.000	8	0.500	0.750
2	0.206	0.370	9	0.519	0.769
3	0.307	0.480	10	0.536	0.785
4	0.370	0.604	20	0.632	0.863
5	0.415	0.656	27	0.667	0.889
6	0.450	0.697	125	0.800	0.960
7	0.477	0.727	1000	0.900	0.990
			8000	0.950	0.9975

Now, in both the cylinder and the lamina the surface forces are the only forces supposed to act, and in each case the surface force is in equilibrium with itself. This is the condition of unstable equilibrium. For, in the first case, if any impressed force, or the addition of any external energy, should cause the liquid mass in the cylinder to move and thus cause the diameter to become less in one section and to become greater in the adjacent section, the liquid would at once accelerate its flow from the former, where the pressure due to the surface force is increasing, to the latter where the pressure is decreasing. This flow would continue until the whole mass was gathered into separate spheres. And in the second case such exterior disturbances would cause adjacent areas to be subject to unequal pressures with consequent mass movements (which are difficult to describe or explain) resulting in the formation of small perforations through the lamina, and the complete breaking down of the lamina into spheres, in the manner to be described later on. This establishes the proposition.

Ideal Case Modified by Physical Conditions. It will be observed that the proposition is true for all diameters of the cylinder and thicknesses of the lamina. In the extreme cases where the cylinder is a row of contiguous molecules and the lamina a single layer of contiguous molecules, there is no reason for thinking that the law would not operate, since it has been shown that the enveloping surface forces are to be considered effective about molecular masses. Such a cylinder or lamina would, therefore, break up into spheres, each containing many molecules, and the actual existence of a monomolecular film of oil would be extremely improbable.

It has been remarked that the tendency is to gather as great a length of cylinder and as large an area of lamina as possible into one sphere. In the extreme case, therefore, an infinite length or area would be gathered into one sphere. But this ideal case, as thus mathematically conceived, cannot actually take place. For inseparably connected with this phenomenon there are always other phenomena, or causes, which act to modify this ideal result, such as attachments

at the ends of the cylinder and at the borders of the lamina, inertia of mass, external and internal heat vibrations, and gravitational, electrical, and magnetic forces.

Idea of a Mono-molecular Oil Film not Confirmed. Now free spheres of unlike liquids always coalesce in the way previously described, regardless of their relative sizes. Thus a very small sphere of oil will, as it were, strive to envelop a large mass of water contained in a vessel, and will, therefore, extend as far as possible over the surface in a thin lamina. It is the opinion at present held by Brillouin, Devaux, and Langmuir, first put forward by the late Lord Rayleigh, that the oil ceases to spread when it reaches a thickness of one molecule.⁸ The writer has not been able to confirm this view. For long before such a condition is brought about the process sets in by which the film of oil suffers either partial or complete disintegration into microspheres. It thus obeys the law of the free plane liquid lamina even though one face is in contact with the face of another immiscible liquid. This disintegration we shall now describe.

IV. EXPERIMENTS

Method of Measuring Small Quantities of Oil. To obtain the requisite small amount of oil use was made of the law of the free liquid cylinder. A small glass fibre about



Figure 2.—Droplets of oil upon a glass fibre.

1/500 cm. in diameter was held at one end by folding it between a piece of gummed paper. It was then drawn through a drop of oil. The oil adhering to the glass as a cylindrical sheath almost instantly formed itself into a succession of

⁸It is a question of fact and not of theory; the experiments of Devaux, Rayleigh, etc., seem to me decisive. Perhaps the quantities of oil used by the author were always too large.—(Note by M. Brillouin).

small droplets with sometimes a secondary action resulting in a series of smaller or sub-droplets between these. (Fig. 2). With a piece of dampened paper all the droplets except one near the end were drawn off. They were ellipsoids of revolution almost spherical and, unless they were very large, the fibre coincided with the major axes. Their dimensions could thus be measured and the volume calculated by the equation

$$V = \frac{\pi}{6} ab^2 - \frac{\pi}{4} a\delta^2, \dots\dots\dots (3)$$

where a and b are the major and minor axes and δ the diameter of the fibre.

Method of Obtaining a Clean Water Surface. For the water surface, a shallow circular vessel of a convenient size (Fig. 3) was filled exactly level and the water surface scraped clean. To prevent water currents and reflection of light beneath the surface the vessel was filled to within a few millimetres of the top with fine gravel stones of a dark colour. Vibrations of the building and currents of air were avoided as far as possible. Fine talc was blown on the surface to render the surface more visible.

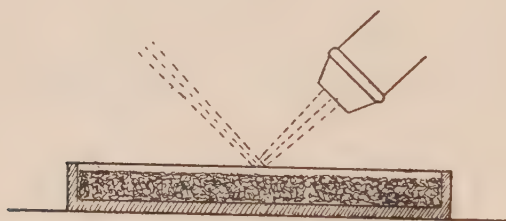


Figure 3.—Method of observing surfaces of fluids.

The Great Violence of the Wave Shock on Contact. The droplet of oil was then carefully lowered over the centre of the surface. At the instant of contact with the water the oil was violently torn from the fibre, the water suffered a distinct tremor or shock, and a tidal wave radiating from the centre swept the surface clean of the talc to the edge of the vessel. The oil seemed to have disappeared completely.

Discovery of Microglobules and their Number. Not so,

however, for when the microscope (power about 90) was directed at the proper angle for the reflected light, a great number of microglobules or spheres of the oil were seen moving in a narrow horizontal zone across the field of view, the upper and lower parts being out of focus. They were also examined with the microscope in a vertical position. They were approximately of the same size and evenly distributed on the hexagonal plan (Fig. 9). Their number, then, could be estimated by the equation

$$N = \frac{\pi}{2\sqrt{3}} \left(\frac{D}{s} \right)^2$$

where D is the diameter of the area cleared of the talc and s is the average distance between successive microglobules. The number of these microglobules varied with the size of the droplet, the kind of oil, and the area to which the action was confined. In general, within certain limits the larger the droplet the fewer the microglobules. If the droplet was small the microglobules were too minute to be seen. The following table shows a few of the many results obtained.

TABLE II

Kind of Oil	Volume in 10^{-6} cm. ³	Area in cm. ²	Number of micro- globules	Average thickness in 10^{-8} cm.
Corn oil.....	98.2	416	5,610,000	24.0
Corn oil.....	81.4	346	26,400,000	23.7
Oleic acid.....	141	491	109,000	28.7
Oleic acid.....	192	491	72,000	39.1
Cod liver oil....	2.22	5.31	21,500	41.8
Sweet olive oil...	32.9	70.9	8,600,000	46.4
Whale oil.....	41.6	70.9	10,600,000	58.8
Lard Oil.....	29.5	63.6	55,000,000	46.8
Paraffin oil	68.6	0.567	1	11,150

Theory Confirmed. Excepting the paraffin oil, which spreads only to a thick disc, these results confirm in a remarkable way the conclusion arrived at in the proposition discussed above. The question naturally arises: by what

process is a particle of oil, not more than 3 or 4 hundredths of a milligram in weight, broken into ten million fragments in a fraction of a second? Here in most cases the area affected by the oil was restricted in some way to render the particles visible. For results given in Table III the area was unrestricted.

TABLE III

Kind of Oil	Vol. in 10^{-6}cm.^3	Area in cm.^2	Average thickness in 10^{-8} cm.
Corn oil.....	7.29	113	6.47
Corn oil.....	15.9	363	4.37
Corn oil.....	1.53	33.2	4.63
Oleic acid.....	2.91	63.6	4.72
Oleic acid.....	1.85	38.5	4.80
Oleic acid.....	12.9	314	4.20
Oleic acid.....	0.178	28.3	.63
Oleic acid.....	1.18	227	.52
Olive oil.....	11.2	201	5.57
Olive oil.....	21.6	284	6.33
Castor oil.....	24.0	284	8.45
Castor oil.....	0.306	9.62	3.18
Castor oil.....	0.606	50.3	1.60

Proof that the Oil Film is Discontinuous. Now the molecule of the common oils ranges about 8×10^{-8} cm. in diameter; that of oleic acid being 10×10^{-8} . From these results and from many others it does not seem possible to infer any relation between the average thickness of the oil on the water and the diameter of the molecule. On the contrary they show conclusively that the oil does not exist on the water as a mono-molecular film or any thicker layer, but in discontinuous masses. These masses are doubtless of the same nature as those observed in Table II. It is reasonable, then, to infer that in the region where the average thickness lies between those given in Tables II and III the oil exists in the form of microglobules too minute to be observed directly.

Thick Films. The following Table shows a number of single stratum films whose average thickness varies from 30 to 2,500 molecular diameters (8×10^{-8}). They were

formed by confining a larger droplet to narrower limits than before. They were at first all continuous, but, as indicated in the table, signs of disintegration soon appeared.

TABLE IV

Oil	Vol. in 10^{-6} cm. ³	Area in cm. ²	Av. Thickness in 10^{-8} cm.
Linseed oil.....	167	70.9	237

(In a few seconds the oil formed itself into the filament of an open hexagonal net-work of a very fine mesh.)

Corn oil.....	390	70.9	550
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(The oil in the central area soon went into an open net-work as before but with thicker threads and larger mesh and in the outer concentric zones it appeared as microglobules which were smaller and more closely arranged nearer the outer border.)

Lard oil.....	478	70.9	676
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(The oil went into thick figure forms separated by wide clear areas of water which nevertheless were sprinkled over with large microglobules of oil formed by secondary disintegration of the edges of the figure forms.)

Corn oil.....	958	17.0	5620
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(At first the colouring, which was absent in the previous cases, was very brilliant. The oil slowly spread out to occupy an area of 30.2 cm. with an average thickness of 3160×10^{-8} , the colours disappearing but re-appearing in figure forms in variegated hues as the film suffered disintegration.)

Lard oil.....	2210	10.8	20,500
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(The film was too thick to show any colours but there were signs of disintegration with colours at the edges.)

Variation in the Law for Particular Oils. Particular investigations showed that the peculiar action of many oils used as ore flotation agents depends on their property of spreading on the water in a thin continuous film that withstands disintegration. Thus certain effective grades of pine oils, composite in their nature, form films that will not disintegrate until their thicknesses are below 15 to 7 molecular diameters. Lower grades of these oils disintegrate at greater thicknesses. In these cases the bubble films are stratified.

The Process of Disintegration. A study of these single

stratum oil films on water reveals the actual process by which the disintegration is effected. It is best to consider such a film as composed of a thin liquid mass held between two parallel surfaces which exert a constant stress to reduce the surface-area, even though one face of the film is attached to the surface of the water. Now two air-spheres in the interior of a liquid water-mass coalesce in apparently the same way as two water spheres coalesce in air. We assume, therefore, that the surface forces in the areas bounding the air masses in this case act in the same way, that is to say, when the last three molecules separate and bring the opposite surfaces into contact in the intervening space, the surface forces unite in the periphery of the common area, and cease to act in the area itself. There will thus be a free opening rapidly enlarging from molecular dimensions in a spherical form, and connecting the two free or gas chambers into one. In a similar way a free liquid cylinder finally reaches a state where the last two molecules are about to separate. The surface force then closing in upon itself between the masses from two directions, both perpendicular to the axis, comes into contact along a line and ceases to act, that is, the cylinder is disrupted. These two laws, or variations of the same law, are seen in constant operation, not only in the case of free liquid cylinders and free simple films, but also when they are attached to a liquid surface of a different substance, and even in the case of a simple film contained between two other films or surfaces of different substances.

THE SIX STAGES IN THE DISINTEGRATION OF LIQUID FILMS

The First, or Lamina Stage. When formed under suitable conditions, the oil rests on the water in a continuous circular mass (Fig. 4) whose thickness diminishes with the distance from the centre. A number of Newton rings contract their diameters, showing that the mass is moving outwards and causing the thickness to become more uniform. Finally the rings all disappear at the centre leaving the whole lamina of oil of approximately one tint.



Figure 4.—First, or Lamina Stage.

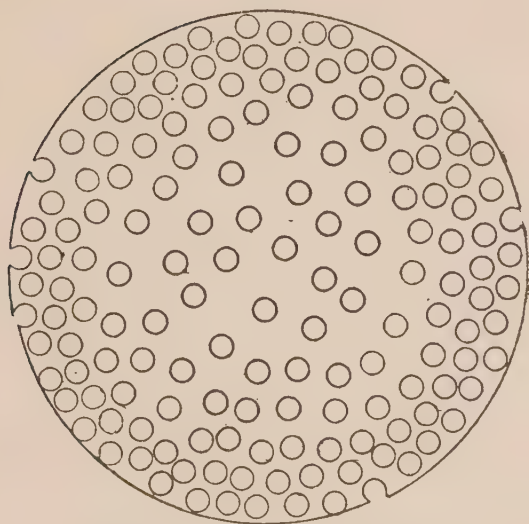


Figure. 5.—Second, or Colander Stage.

The Second, or Colander Stage. When the thickness is uniform many small reddish purple spots begin to appear over the lamina, rather more thickly distributed towards the border. These grow in distinctness and become surrounded by one or more colour rings. Afterwards in the centre of each spot a clear, dark, circular opening (Fig. 5) through the oil lamina gradually increases in width as the oil is gathered from the water by the united action of the upper and lower surface forces. The oil thus forms a thick ring-like mass about the clean water circle, and, before it has time to distribute itself in the surrounding area, is formed by the law of the liquid cylinder into a regular succession of mounds (Fig. 13) resembling somewhat a necklace of pearls. These mounds were the brilliant droplets which Perrin describes as bordering the black spot areas in the soap film. The whole lamina, then, like the bottom of a colander, is actually filled full of circular openings.

The Third, or Figure Stage. As the circular openings grow larger, the oil between two circles is compressed into a narrow cylindrical mass, which is disrupted as described previously and the projecting ends are pressed into the larger triangular masses on either side. This action is generally attended with a violent shock when the powerful surface forces are required to make a sudden new adjustment of their areas. In this adjustment the oil masses are rapidly shifted to new regions, the two circular openings are changed into one larger circle, and the other openings near by moved into new positions. This readjustment continues with decreasing power until another disruption suddenly causes movements in other unexpected directions. This action of joining the open water areas by disrupting the narrow oil threads continues until the oil is all gathered into a number of peculiar figure-forms (Fig. 6) so often seen on oily water. The processes of the second and third stages often proceed simultaneously, where figure-forms already isolated make new openings (Fig. 15) that break into each other or into the surrounding open water and subdivide the oil into smaller forms.

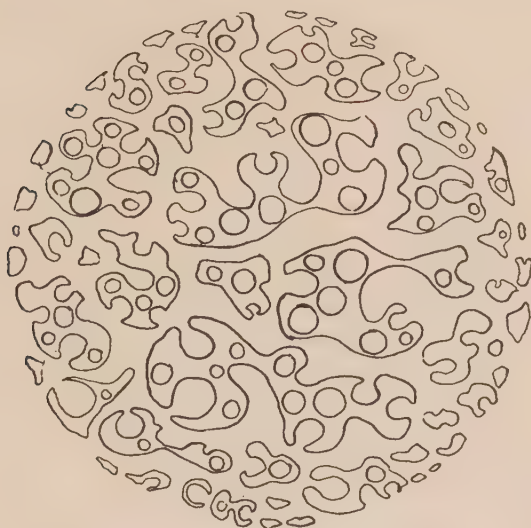


Figure 6.—Third, or Figure Stage.

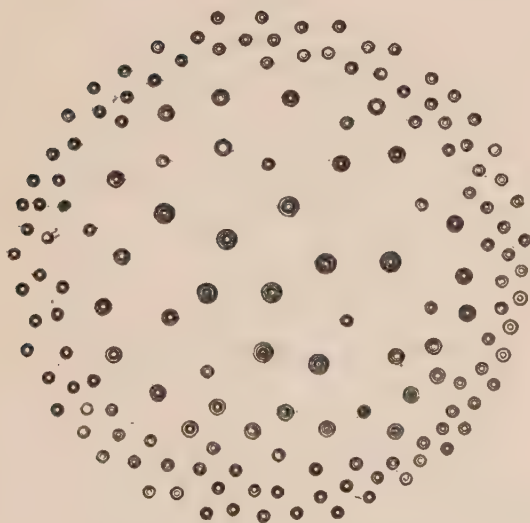


Figure 7.—Fourth, or Disc Stage.

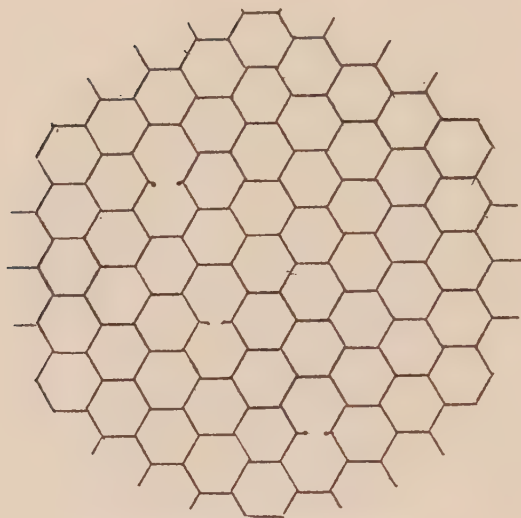


Figure 8.—Fifth, or Net-work Stage.

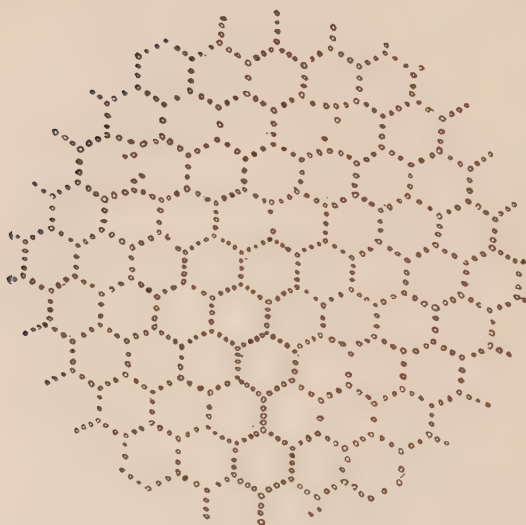


Figure 9.—Fifth Stage : Beaded Net-work.

The Fourth, or Disc Stage. These figure-forms, when the oil is not too great in quantity, by continued subdivision and by reducing all irregular projections, finally become circular in form (Fig. 7). If they are very small, they remain globular; but they generally become thin discs having one or more concentric colour rings or areas differently tinted. They are generally larger and farther apart in the central areas than in zones more remote.

The Fifth, or Net-work Stage. Frequently, however, the cylindrical masses between the pairs of enlarging circles, instead of being disrupted, lengthen out into straight filaments and connect the diminishing triangular masses into a beautiful hexagonal net-work (Fig. 8) extending over the whole area. Occasionally one of these filaments breaks and causes the system to readjust suddenly its forces to new relations. The two hexagonal areas tend to become a larger octagonal area while those adjacent to it accommodate themselves to the new form. By repetitions of this process, the original hexagonal net-work often deteriorates into an irregular pattern with larger open spaces. In some cases the disruption even goes on until the net-work is divided into a number of separate figure-forms which change slowly into discs. More frequently, however, the filaments becoming uniform in diameter suffer division into small globules, apparently in the same way as the liquid cylinder forms itself by its enveloping force into spheres. These globules are fairly uniform in size and evenly spaced, and for a time the whole surface appears covered with an open net-work (Fig. 9) where the filaments are like chains of pearls. The picture is singularly beautiful.

The Sixth, or Microglobular Stage. The discs and the larger globules of the last two stages repeat (Fig. 12) one or more times on a smaller scale these successive stages of disintegration into smaller parts which, instead of expanding into discs, contract into spheres or thick globules. These are the microglobules of Table II (Fig. 10). They are darker in appearance than the discs and reflect light from their convex surfaces, by which means they are recognized. When small,

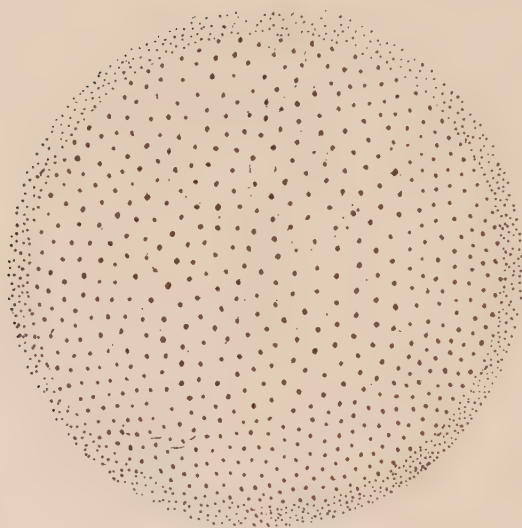


Figure 10.—Sixth, or Microglobular Stage, showing the result of depositing successively a secondary and a primary doublet.



Figure 11.—Enlarged portion of Fig. 10, showing the disturbing effect of the Brownian movement.

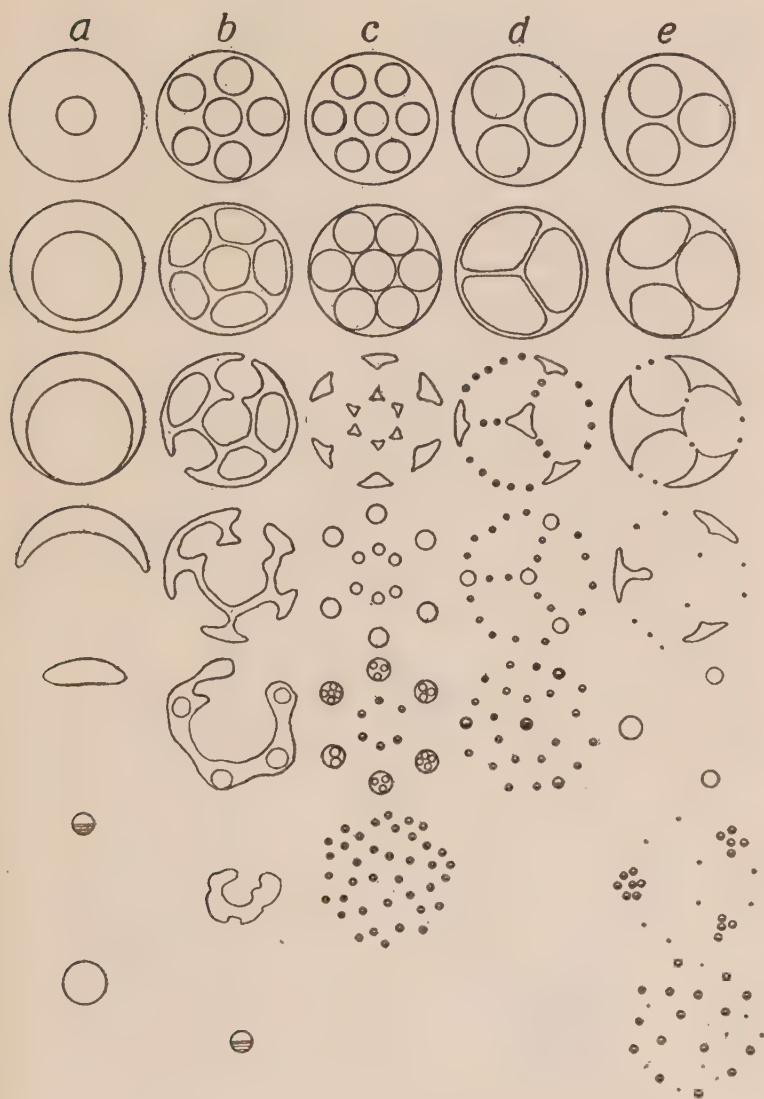


Figure 12.—Various phenomena observed in secondary disintegration: (a) and (b) in oleic acid; (c) in corn oil and lard oil; (d) in olive oil, gasoline and cotton-seed oil; (e) showing microglobules of unequal sizes.

they are seen knocked about by the Brownian movement, (Fig. 11), and for this reason are unable, even when they are large, to maintain fixed relative positions for any length of time. The chain net-work is soon disarranged and often small microglobules invade the wide clean areas between the large ones.

Variations in the Stages. These six stages are not to be regarded as distinct from one another. Two or three may in fact be going on at the same time. Also they vary greatly in character with the kind and amount of the oil, with the kind of water, and even with the different grades of the same oil. Many liquids not usually classed as oils, as coal oil and turpentine, disintegrate in the same way. Other evaporating liquids, as gasoline, chloroform, and benzene hasten the process by evaporation, while one at least, paraffin oil, disintegrates very slowly and with difficulty.

Oil dissolved in Benzene. A very delicate test for pure benzene consists in allowing single drops in succession to spread out and evaporate on a clean water-surface. Talc is sprinkled on the surface before each drop is deposited. If the successive drops behave in the same way, and leave no whitish streaks or patches, the sample is pure. Thus a drop of a solution of 1 part oleic acid to 1,000 parts of pure benzene spreads out in great agitation, disintegrates into irregular areas, and evaporates without leaving any visible trace of oleic acid. The second drop does not spread so violently. The third or fourth experiences more difficulty, spreading only into a thick circular lamina, and gathering itself as the evaporation proceeds into four or five small globules or discs at the border. In a little while these globules one after another shoot out with great speed and disappear at the ends of their paths, leaving visible whitish streaks on the surface of the water. Finally a large drop remains stationary as a globule from which the talc slowly recedes. The microscope reveals disintegration proceeding at the edges from which small microglobules are being projected into the open space around. Near the end of the evaporation the mass takes on a rapid irregular motion, clearing a wide path for itself

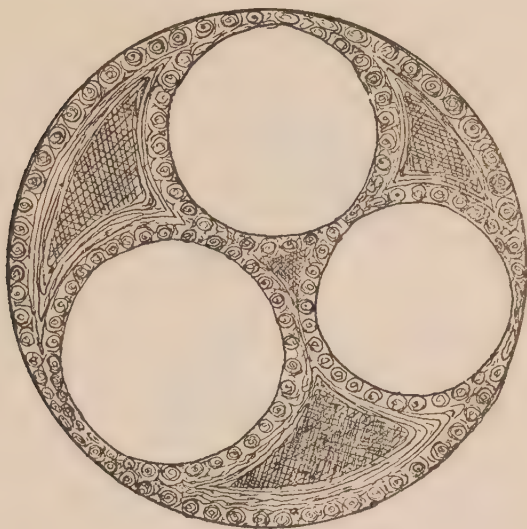


Figure 13.—Details of secondary disintegration, showing three colander holes fringed with mounds.

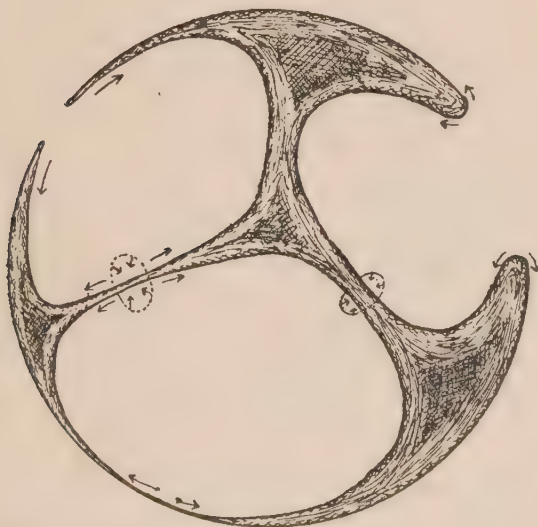


Figure 14.—The same as Fig. 13, showing motions of liquid.

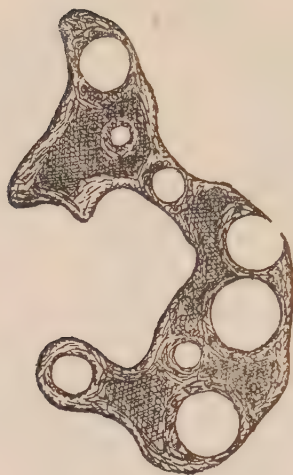


Figure 15.—Detail of a form represented in Fig. 6.

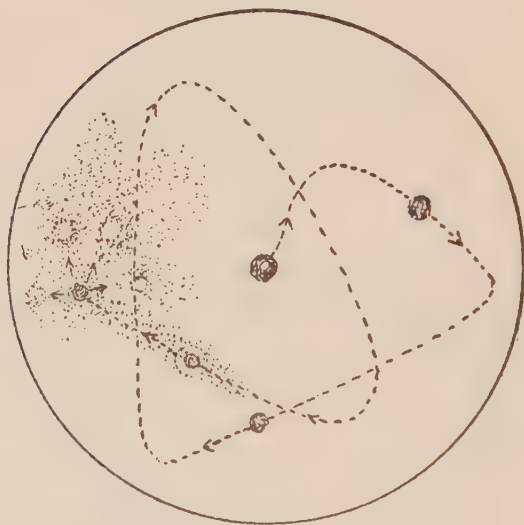


Figure 16.—Action of a Drop of Solution of Castor Oil in Benzene on Water.

through the talc. It then halts, spreads out, and goes through the stages of disintegration peculiar to pure oleic acid. A search afterwards reveals the whole surface not covered by the talc to be dotted irregularly with microglobules.

If castor oil be used instead of oleic acid (Fig. 16) the globular disc near the end of its path spreads out and explodes into three or four smaller parts which again suffer explosions and disappear, leaving a great number of microglobules distributed in whitish streaks and patches.

In the light of these observations and in the extremely violent action that accompanies the spreading, and that extends far below the surface, it is difficult to see that the methods adopted by Rayleigh,⁹ Devaux,¹⁰ Langmuir,¹¹ and others for obtaining a thin film of oil by allowing a drop of a solution of the oil in benzene to spread on water, can give a continuous mono-molecular film of the oil, or that any inference can be drawn as to the size and shape of the oil molecules. It is evident also that some other explanation must be found for the sudden changes in the surface forces first noticed by Lord Rayleigh in 1899.

V. THE SOAP BUBBLE

The Constitution of the Soap Bubble Film. The complex phenomena of the soap bubble may now be explained. The spherical emulsion-forms of the soap solution may be seen on the surface of the liquid, when magnified from 100 to 250 diameters, spread out as flat discs and overlapping. But, when an air bubble is formed, all the liquid solution between the two air masses is near, or next to, the air surfaces; and the number of flattened forms is increased, and their width greatly extended. These flattened forms overlap one another and are attached at their edges to the sides of the vessel, and to the spherical forms in the liquid at the sides; and they thus form a stratified film of great strength and

⁹Investigations in Capillarity, *Phil. Mag.* S. 6, Vol. 48, p. 331, 1899.

¹⁰*Review of Papers, Smithsonian Institution Publications, Physics* p. 261, (1913).

¹¹*Loc. cit.*

durability, the strength being somewhat uniform on account of depending on the attachments rather than on the thickness. Between these flattened forms are thin masses of water which constantly drain out by gravity to the lower parts. While many forms are thus flattened, many others remain as high mounds that slip down the slope outward from the central area. These may be distinguished by their showing in a little while two or more colour bands. The regular downward motion of these mounds is greatly interfered with by their being knocked about in various directions by the molecules of the air. These irregular motions may be increased by holding near the film a drop of some evaporating liquid such as benzene, and diminished by enclosing the film within a confined space.

The Permanency of the Soap Film depends on the Slowness of the Disintegration of the Separate Strata. Each flattened disc or single stratum next the air, and probably an interior stratum also, soon begins to go through the regular stages of disintegration as previously described. Dark purplish spots grow into circular areas having a uniform colour. These are the colander holes through the stratum. They at once begin to move upwards and soon resemble in form tadpoles with their tails turned away from the central area. Then in the next stratum within the tadpole areas one and sometimes more circular black-spot areas appear, which are thus moved nearer towards the centre. The thicker flat masses between the tadpole areas move outward and downward but not so fast as the ring-mounds. They pass from a yellow to a faint whitish tinge, and soon become pierced with many colander holes. These holes with the tadpole black spots form the black spots of the third and fourth degrees according to Perrin's notation.

The Sudden Readjustments of the Film Masses. The speed of the disintegration increases. The colander holes break into each other by snapping the threads or isthmuses between them. The soap masses rush along the wider isthmuses into the triangular masses. The projections are rapidly reduced. The central black spot area, by the addition of

many smaller ones, some of which have travelled from the outer border, is greatly increased. Upon this black-spot area the various figure forms may be seen changing into discs and moving down the slopes. Frequently (Fig. 12) these discs disintegrate into one or more globules moving irregularly on the black-spot area,—into *one* when the discs undergo the process unsuccessfully (Figs. 12*a* and 12*b*). Meantime, in the thicker portions of the film with its moving tadpole areas, high ring-mounds, and flat areas, an isthmus between two colander holes in an interior stratum may break, and the various surface forces in adjusting the altered strain, jerk these visible forms about in motions impossible to describe.

The Necklace and Mound Formations. As in the oil film on water, the isthmuses may form themselves into threads which become the filaments of a net-work supported by the black-spot area. On a number of occasions this net-work remained long enough for the threads to form themselves into necklaces of microglobules. Often an exterior stratum of a large black-spot area is removed by forming in itself only two colander holes between which the thread remains stretched across the area until it goes into a row of microglobules. Again the stratum may be drawn off by forming only one colander hole. In this case, and in some others also, the liquid in the interior of the emulsion-form composing the stratum is gathered into a thick ring-like mass (Fig. 8) surrounding the opening. This mass, as was observed in the oil film, goes into a succession of mounds (Fig. 15) that persist for some time, and serve to mark the boundary between two degrees of blackness. These mounds are not to be confused with the microglobules formed from the filaments. They were both observed by Perrin, but only the latter appear to have the Brownian movement.

The Collapse of the Soap Bubble Film. Observations of the air bubbles in the vats of the flotation processes for the separation of mineral ores, as well as of those bubbles produced in the laboratory, show that the immediate cause of the collapse of the bubble in most cases is the rupture of the isthmus or thread between two colander-openings, as pre-

viously described. In certain carefully prepared soap-solutions which are designed to prolong the final black-spot film, the disintegration of the separate strata is exceedingly slow. It is probable that the water is practically all drained out between the final two or three strata before this is accomplished. The final stratum may then, on some slight exterior disturbance, proceed to form a colander-opening which, since there are no resisting attachments, enlarges with great speed. If the bubble is spherical, this speed is so great that the ring-like mass accumulating in the edges of the opening is unable to follow the curvature to the base of the bubble, and is thrown off tangentially in separate mounds or spherical masses. This phenomenon has been erroneously attributed to the elastic expansion of the enclosed air when the pressure induced by the tension of the film is suddenly relieved. Such a force is altogether too small to account for it. In the case of certain compound oils on water, the film so changes its constitution by evaporation, before disintegration sets in, that it acquires the properties of a solid, breaking like a pane of glass. It is possible that an analogous process occurs in the final stratum of the black area when it persists for a long time.

The Thickness of the Final Stratum. It has been shown that in the mass of a pure liquid no molecular attraction is to be considered, nor is there any surface-force enveloping the individual molecules. Consequently, there is no reason to regard the liquid molecules as spherical. Likewise in the thin interior mass composing each stratum of a soap-film, the different molecules are subject to no attraction or exterior pressure, and thus are free to accommodate their forms to one another, having respect only to surface forces between contiguous unlike molecules. Now a film composed of three layers of perfectly rigid spherical molecules of diameter d has a thickness of $\pi d\sqrt{6}$, or of 2.45×10^{-7} cm. for oleic acid. If the molecules accommodate their forms so as to occupy *all* the space between two parallel planes, the film will have a thickness of $\pi d\sqrt{3}$, or of 1.81×10^{-7} cm., which is a little

less than twice the diameter of the molecule and which agrees with Perrin's value of 1.9×10^{-7} cm. Yet, even so, the flattened emulsion-stratum may be composed of molecules which are themselves like flattened globules or discs adhering to each other. The thickness, then, would depend on the extent of this molecular flattening, which would in turn depend upon the strength of the surface forces between unlike molecules and of their attachments. There would thus be no reason for thinking that a single stratum could not have an actual thickness of one molecular diameter while still preserving its constitution as a permanent emulsion-form.

There still remains the question of why the oil spreads on water, or why the soap extends in stratified form on the air-surface of its solution.

VI. SUMMARY

The surface energy rendered available as heat by the natural coalescence of liquid spheres is found to be precisely the latent heat of condensation where the spheres are the free molecules of the gas. This leads to the belief that surface tension is an elemental force which may be described as a *tendency to lessen* the closed boundary of a free molecular mass and the boundary separating the contiguous unlike molecular masses. This enables molecular phenomena to be studied from a new point of view quite different from that of molecular attraction.

The breaking up of projected cylindrical streams and thin sheets of liquids into spheres is proved mathematically to result from the sole action of this force.

By a new method of depositing a small measured particle of oil directly on water and by a simple and more comprehensive way of observing the transformations occurring on the surface, it is shown that all thin oily films on water conform to this law and disintegrate into microglobules. The actual existence of a mono-molecular film of oil on water is disproved.

A detailed description is given of the processes by which the films were observed to disintegrate.

The stratified structure of the films of the soap bubble is shown to result from the lateral expansions and attachments of emulsion-forms in a thin layer of the solution of soap separating two air spaces. The formation of the black spot with its degrees of blackness and all the strange movements and play of colours that precede it result naturally from the successive disintegration of the separate strata according to the same law.

SOME NOTES BY M. MARCEL BRILLOUIN

Avogadro's Number, Heat of Vaporization and Surface Tension (pp. 142-3)

In 1867 the late Professor Ath. Dupré, of the Faculty of Sciences at Rennes, obtained, by analogous considerations, the number 2.25×10^{20} , referred to one cubic millimetre of water, which gives too large a number viz., 4×10^{24} molecules of water per gram-molecule.

This number was obtained by comparing the surface tension, called the force of reunion (*force de réunion*), with the total work of disruption, evaluated either by aid of the internal energy or by the aid of the heat of vaporization furnished by the experiments of Regnault.

These researches were gathered together, after publication in the *Annales de Physique* from 1864 to 1868, into a volume which appeared in 1869 (Paris, Gauthier-Villars), under the title, *Théorie mécanique de la Chaleur*.

The determinations of *attraction on contact* occupy all of chapter viii, which still appears to me to-day to be an extremely remarkable research in physical chemistry. The number quoted is reached at the end of chapter ix (p. 403-404), which is scarcely less interesting than the former.

Nature of the Molecular Forces (p. 143)

The reasoning developed in this paragraph does not appear to be very clear from a mechanical point of view. Surface tension is reducible, as we know, to mutual actions between molecules. It seems difficult to treat it as an action of elementary and ultimate nature—irreducible to mutual actions of a character more or less Newtonian—and operating about molecules whose great complexity of discontinuous structure is now well known. But the physical chemists, especially those of the new world, often make a happy use of language which could not be used by minds accustomed to precision.

Limits of Stability (p. 146 et seq.)

One can employ two principal methods for the discussion of stability.

1. The one familiar to mathematicians and employed by Plateau, which consists in comparing the possible permanent state of which one seeks the stability to the different states disturbed infinitely slightly; and to determine either the sign of the variation of potential energy, or the value of the proper period (real or imaginary) of the oscillations produced by the disturbance.

By this method Plateau found that the cylinder becomes unstable when its length attains (and exceeds) the perimeter ($2\pi R$) of its right section—a result which is in excellent agreement with all of his observations.

2. The second method consists in comparing two very different possible states and in asking which is the more stable, by a comparison of the potential energies; this is the method employed by Mr. Wilson Taylor. The limit of the length obtained, $\frac{9}{4} (2R)$ is much narrower

$$\left(\frac{9}{4} = 2.25 < 3.14 = \pi\right)$$

than that of Plateau. It applies then only in the case where the cylinder is exposed to violent perturbations (an interesting case of which is the comparison with the limits of stability by expansion of vapours without ions or dust particles, with the ordinary limit of boiling).

For thin films, spherical or plane, the first method applied by Plateau (t. II, ch. IX, p. 172-174), shows that the stability *for small perturbations* is complete, whatever may be the ratio of the thickness to the diameter. This result is very different from that given by the second method, for violent disturbances.

ARTICLE X

THE ACTION OF TWO DROPS OF DIFFERENT LIQUIDS WHEN BROUGHT INTO CONTACT

By means of glass droppers with curved ends I caused two drops formed from unlike liquids which were immiscible to come into contact. The liquids were chosen from water, mercury, oils of various kinds, alcohols, benzene, turpentine, coal oil, carbon bisulphide, gasoline, and others. In every case, as with drops of like liquids, the drops of liquids X and Y suddenly were jerked together, and, when free from contact with other masses, took the form of a sphere. During the first stage of the action the small contact area A still retains a small amount of potential energy in the force-area separating the masses, measured by $F_{xy} \times A$, while the two spheres give up a much greater amount, $A(F_x + F_y)$. The decrease in potential energy, when coalescence takes place, is $A(F_x + F_y - F_{xy})$. There is nothing, however, to hinder the transference of this potential energy into heat until the one mass envelops the other completely. The mass having the weaker area-force surrounds the other. In the case of immiscible liquids I found no experimental exception to this completed action, and in many others the enveloping action was very pronounced before the mixing took place at all.

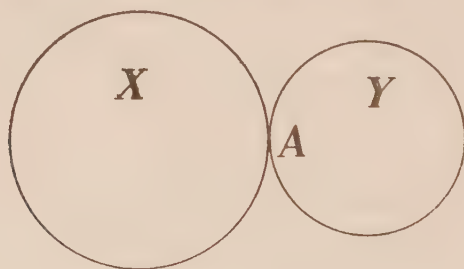


Figure 1

Let d_x and d_y be the diameters of two liquid drops formed from unlike liquids X and Y ; T_x and T_y their area-tensions

next the air; M_x and M_y their masses; and A_x and A_y their areas. Also let T_{xy} be the tension of the area-force between the masses on contact, and A_{xy} the exterior area after coalescence.

Then $d_{xy} = (d_x^3 + d_y^3)^{\frac{1}{3}}$ and $A_{xy} = (d_x^3 + d_y^3)^{\frac{2}{3}} \cdot \pi$.

The conditions which bring about coalescence, T_x being greater than T_y ,

are $T_x - T_y > T_{xy}$

and $d_x^2 \cdot T_x + d_y^2 \cdot T_y > d_x^2 \cdot T_{xy} + (d_x^3 + d_y^3)^{\frac{2}{3}} \cdot T_y$.

The decrease in potential energy of the force-areas

is $\pi \{ d_x^2 \cdot T_x + d_y^2 \cdot T_y - d_x^2 \cdot T_{xy} - (d_x^3 + d_y^3)^{\frac{2}{3}} \cdot T_y \}$.

Thus, if two drops of water and mercury, of equal diameters d , be caused to touch each other, they will coalesce, the water forming an enclosure about the mercury. They will do this if the mercury is clean—a condition hard to obtain on account of a strong tendency of foreign particles to attach themselves to its surface. Here

$$T_m = 540, T_w = 75, \text{ and } T_{mw} = 418;$$

so that the decrease in potential energy in this case is

$$\pi d^2 (540 + 75 - 418 - 2^{\frac{2}{3}} \cdot 75) \text{ or } 57\pi d^2,$$

which represents the amount of heat energy generated by the act of coalescence.

In the diagrams the different stages of the act of coalescence are shown. The small area A (Fig. 1) enlarges and becomes a circle of invasion CD (Fig. 2) which completely spreads over the surface of the drop X , disappearing as the force-areas separate, as in Fig. 3, and take their final positions, as in Fig. 4.

This arrangement of the two drops of immiscible liquids after coalescence is a permanent one; that is, energy would have to be supplied to change the arrangement. The whole, however, may be broken up into two smaller spheres by a blow, but each part will in general be of the same arrangement as before, that is, a mass X will be within a mass Y . A part of the outer mass may also be detached without enclosing a part of the inner mass, while the inner mass may be

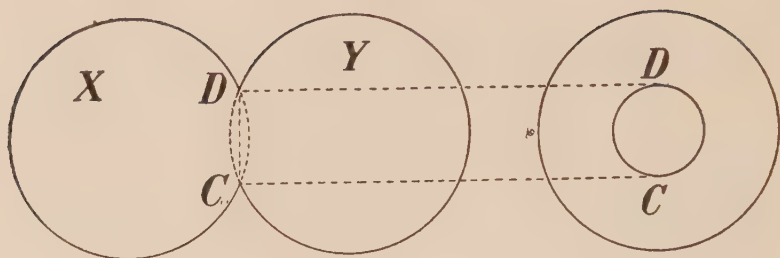


Figure 2

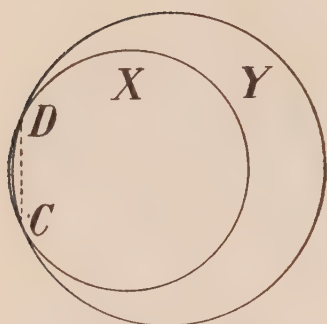


Figure 3

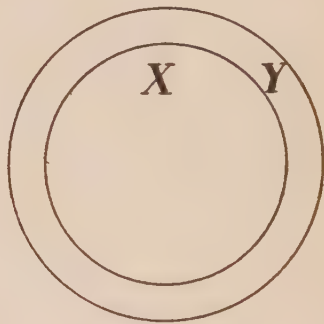


Figure 4

temporarily divided into two or more enclosures lying side by side within one enclosing sphere. If a number of these smaller spheres are lying side by side within a single larger enclosure in a more or less permanent form, we have the essential conditions of an emulsion.

Now it is a universal phenomenon, for I have not found a single exception among the thousand experimental trials I have made, that:

When two area-force enclosures of any substances whatever come into contact, the force-areas unite by giving up the greater part of their surface potential energy in the contact area. Thus if A is the contact area, the potential energy given up is $A(T_x + T_y - T_{xy})$. If one area-force enclosure is about a *solid* mass, the liquid drop, when contact is made with the solid, is at once "jerked" towards the solid mass. It comes to rest

only when a minimum amount of potential surface energy is reached.

There are two characteristic modes of reaching this minimum. (a) If the tension of the area-force about the liquid drop be less than that about the solid, the liquid will spread over the solid surface as though it would enclose it. In this case it is usual to say that the liquid *wets* the surface. Thus a small drop of pure water will surround a clean glass marble; and oil will spread over clean metal surfaces. (b) If the tension about the liquid drop be greater than that about the solid, the conditions are such that the solid should envelop the liquid, and being prevented by the internal forces of the solid goes as far as possible in the process. The liquid drop then stands out in a very convex form with a distinct angle between the surface of the liquid and that of the solid. Then it is usual to say that the surface of the solid is unwetted by the liquid. Thus, mercury will not wet a glass surface, nor water a wax surface or a surface of pure lead.

ARTICLE XI

THE FLOTATION OILS

Recent investigations by the writer into the laws governing molecular phenomena, appear to have an important bearing on many industrial problems. One of these problems is the action of certain oils in the flotation processes of mineral separation. The more theoretical development of these laws may be found in the *Philosophical Magazine* for June 1921. This simple, but hitherto unsuspected, action of molecular forces has a peculiar interest to the engineer in connection with those problems which more and more are now engaging his attention. Until recent years his problems were mainly those that have to do with the force of gravity. During the last ten or twenty years his attention has been chiefly directed to the problem of electrical energy and its distribution. The laws governing these two fields of natural phenomena are fairly well known, so that the engineer may proceed with some certainty to a desired object. But the laws governing the phenomena of molecular action are still little understood. Thus, it is not known why certain oils may be used in the flotation process and certain others cannot; or why sulphides, but not oxides, of metals can be separated by flotation.

The experimental data which are constantly accumulating in the various branches of industrial research have, it is true, been classified to some extent in certain empirical laws, but there does not seem to be any comprehensive and simple theory at present available by which these data may be explained. The only theory that has been used for this purpose is Laplace's famous hypothesis of molecular attraction, which is a modified conception of gravitational attraction, where the actual force is much more powerful, but effective only in a restricted range. The point of view, however, suggested to the investigator by this hypothesis is, unfortunately, an altogether misleading one and has perhaps been rather a hindrance than a help to him. Thus, a hundred years of study of the tension in the surface of a liquid has yielded

nothing except improved methods of determining its magnitude. Its real nature is as much of a mystery as ever, notwithstanding Laplace's explanation on the basis of unequal mutual attraction of molecules near the surface. Again, such an engineering problem as to where, and in what form, the energy which is known as the latent heat of evaporation exists after water has been converted into steam is still unsolved. All we know is that the energy disappears and returns again when the steam is condensed into water. A clear understanding of this latent or "lost" energy would probably have shown whether it is economically possible to manufacture fuel from water-soaked peat or not, and the recent efforts by the Canadian government to solve this question might have been avoided, or the research conducted with a fuller knowledge of natural laws. The real part which the water molecule plays in Nature's economy is little understood, and there is no doubt that a fuller knowledge of it would be of immense value in the study of climatic conditions, in agriculture, and in various other fields of investigation.

Without going too far into the theory of molecular force, which may be read in detail in the writer's publication mentioned above, it will be sufficient to say that it has been proved that the true conception of molecular action is to be found by observing "the coalescence of two free drops of water", a phenomenon with which nearly every one is familiar. No action can take place unless the drops are brought into contact, and then their coalescence is almost instantaneous. The force which causes this is not a force "attracting" their masses, but it is a force "enveloping" their masses. These forces are fundamentally different from each other. The former lessens the distance between the centres of the two masses (Laplace's hypothesis); the latter lessens the surface area required to envelop the masses. The former acts at all distances, or, at least, at certain restricted distances; the latter acts only when the two masses come into contact.

Again, by virtue of the tendency of this force about every mass to contract the enveloping area, this area possesses a definite amount of potential surface energy, the amount

per unit of area depending on the kind of mass and not on the amount of mass. When, therefore, two free masses come into contact, the enveloping forces unite so as to enclose both masses in one enveloping force. In doing this the total free surface about the masses is diminished in extent; and, consequently, the potential surface energy is reduced, that is, it is changed into heat energy. This action, then, is another example of the thermodynamical law that the potential energy of a system tends to decrease to a minimum. The motive for all molecular action is to reduce the potential energy of the system through the action of the enveloping force of surface tension. The law extends from visible masses to the invisible molecules of a gas or a liquid.

The writer has made some comparisons between the magnitude of this force and that of gravity, and found that, for molecular distances and masses, the enveloping force is inconceivably (10^{32} times) greater than the force of gravity. It is also quite distinct from, and of the same order as, the force of electrical repulsion or attraction under the same conditions. The enveloping force is about one-half as great as the repulsion between two negatively ionized molecules of water nearly touching; the former being 2.10×10^{-5} and the latter 4.62×10^{-5} dynes. A free water sphere 1/10 of a mm. in diameter is under a pressure of about 3 per cent. more than the atmospheric pressure by virtue of its surface tension, but a water molecule is under a pressure of about 13,000 atmospheres from the same cause.

Another comparison may be interesting. Taking the rainfall in the Niagara Peninsula as 30 inches, to water a garden plot 30 by 40 feet it requires on the part of the sun an expense of energy equivalent to that of an engine of 1,500 horsepower working night and day throughout the year to load the water molecules with the necessary energy and float them in the air from the water surfaces of the lakes and seas. To supply the moisture necessary to grow a British Columbia fir tree it would be necessary to keep such an engine working continuously for two hundred years.

From the study of the coalescence of two spheres of the same liquid it is easy to pass to the study of the coalescence of two spheres of unlike liquids, then of a liquid and a solid, and finally of two small particles of solids. The inference by induction from thousands of observations made during several years is that the same act of coalescence always takes place, the same enveloping force tending in the same way to reduce the total potential surface energy of the two free masses coming into contact, though in the case of the solid particles the resultant forms are not spherical. The following varieties occur:

(a) Of two immiscible liquids, the mass of the one sphere immediately surrounds the other as a concentric shell.

(b) Of two miscible liquids, the mass of the one sphere immediately surrounds the other, and afterwards diffusion of the molecules of the liquids takes place more or less rapidly until the resulting sphere becomes a solution.

(c) Of a liquid and a solid, sometimes the mass of the liquid immediately surrounds the solid as a sheath, in which case the liquid is said to "wet" the solid; or, the action is in the opposite direction, as though the mass of the solid would surround the liquid, but, being unable to do so, the liquid stands out as a convex globule attached to the solid. In this latter case the liquid is said not to "wet" the solid.

(d) Of two solids, two particles, if small enough, will always attach themselves to each other. This attachment is caused by the enveloping forces uniting around a small contact area which has yielded up some or all of the potential surface energy which the contact surfaces carried before coming into contact. This is the cause of the flocculation of finely ground particles which often interferes with the separation of the small mineral particles from the gangue. It is the cause of the molecules of a gas condensing on the surface of glass and of penetrating the small openings of a porous solid. As the solid particles become larger, gravity and other causes act to overcome this attachment and to obscure the action of the law in this case.

As to why, of two immiscible liquids A and B , or of a liquid A and a solid B , the liquid A should envelop B instead of B enveloping A , the writer has not been able to determine from observation any rule that applies. In general, of two liquids the one with the weaker surface tension envelops the other, but in practice it is easier to ascertain which way they act by trial than to depend on measuring their surface tensions. Besides, in case one substance is solid, there is no practical means of determining what its surface tension is.

It was observed also that the coalescence of liquid spheres or the attachment of solid particles takes place independently of the relative size of the free masses that come into contact. An important case of this is the action of a small sphere of oil when brought into contact with the surface of a large mass of water. The mass of the oil tends immediately to spread out over a wide area as though to envelop the water sphere the size of the earth. Various views are held concerning the nature of this "film" of oil thus formed on the water, the most common of which is that suggested by Lord Rayleigh and adopted by Devaux and Langmuir, that the spreading ceases when the oil has reached a single layer of contiguous molecules. The writer has not been able to confirm this view of the existence of a mono-molecular oil film either experimentally or from the theory of the enveloping force. For the details of these experiments and proof the reader is referred to an article on *The Structure and the Disintegration of Liquid Films*.¹ The following are the chief conclusions arrived at from these observations:

When a small droplet of any oil (with probably only one exception) is deposited on a clean water surface,

(1) A distinct and powerful shock is given to the surface, sufficiently strong to send a tidal wave to the whole circumference of the water.

(2) A large circular area is swept clean of any floating particles, such as talc, previously dusted on the water.

(3) Over this clean area the microscope reveals a great

¹Vide Art IX, p. 142.

number of very small spheres (microglobules) of oil of nearly uniform size evenly distributed over the whole surface.

(4) If the area is restricted so that the average thickness of the oil is great, these microglobules become larger and may even be seen by the naked eye. If the area is not restricted, the oil clears off a large area over which the oil, if evenly distributed, would form a "film" whose average thickness would be only a small fraction of a molecular diameter; but over which, in reality, it exists as evenly distributed microglobules too small to be observed with the microscope.

(5) The appearance of the act of spreading would indicate that the disintegration of the oil occurs at the edges of an expanding circular layer and the microglobules are projected radially, by some force underneath, over a large area beyond the circle where the oil is continuous.

(6) An important stage in the disintegration is that where, by restricting the area, the oil spreads in a continuous layer over the whole surface and then goes into an open hexagonal net-work of which the oil is the filament. In this state, as well as in the microglobular state, the area occupied by the oil may be expanded or contracted without breaking the filaments or injuring the microglobules, though in the latter case it was observed that when the area was expanded the microglobules were sometimes further subdivided. It was also observed that the continuous layer of oil possessed these expansive and contractile properties.

(7) But the oils which are derived from the pine and eucalyptus trees disintegrate only when these layers are extremely thin, either into an open net-work or into microglobules. When the layer of oil is made thick by confining the area over which the small quantity spreads, it becomes a tough continuous film having expansive and contractile properties. It does not, beyond a certain thickness, break up into globules as all the other oils do. There is no doubt that it is this peculiar property possessed by the pine oils and other derivatives of the pine tree, such as the creosote oils, turpentine and coal tar, and the oil of the eucalyptus tree, that

enables them to form the froth structure so necessary in the flotation processes. The amount of other oils which are mixed with the pine element regulates in a large degree the effectiveness of any particular oil for that purpose. It is, therefore, important that some means be devised to ascertain just what effect these other oils have in these mixtures, and the following is an attempt to answer this question.

By a knowledge of the laws of coalescence and disintegration of liquids the writer succeeded in isolating very minute particles of oil, so that their dimensions could be accurately determined under the microscope. To a large degree these dimensions were under control, so that suitable small amounts of oil could be isolated and handled. The unit of volume employed was a cube whose edge was one-tenth of a millimetre, a quantity just visible to the eye. For measuring molecular dimensions the Ångstrom unit was used, which is 10^{-8} or one hundred-millionth of a centimetre. The diameters of the molecules of the various substances are from 3 to 14 of these units, and we have chosen for convenience the diameter of the eucalyptol molecule, which is 8 of these units, to express the thickness of the oil films on water. The quantities of oil thus isolated were much less than those employed by Lord Rayleigh, Devaux, and Langmuir, who obtained theirs by dissolving the oil in pure benzene. A number of shallow circular vessels, varying from 6 to 40 cm. in diameter and having their upper edges level, were filled with water a little above the level. A strip of newspaper about an inch wide was then passed over the water surface to clean off any oil or dust particles from it. To prevent reflection of light from the bottom of the vessel and render the surface more visible, the water was coloured with a little methyl violet. It was found by trial that this had no effect on the action of the oil on the surface. Before the oil droplet was deposited a light sprinkling of very fine talc was blown on the surface, which served to determine the shape and extent of the area swept clear by the action of the oil.

If permanganate of potash, however, was used to colour the water, while it was found to have no effect on the action

of the ordinary oils on the water, it completely changed the character of pine and eucalyptus oils, when, or soon after, they spread on the surface. Whether the oil existed on the surface as microglobules, as filaments of an open net-work, or as a continuous elastic film, it was changed into an insoluble solid. If the oil existed on the surface as microglobules with interspaces, the area could be both reduced and increased in extent; if it existed as the filament of an

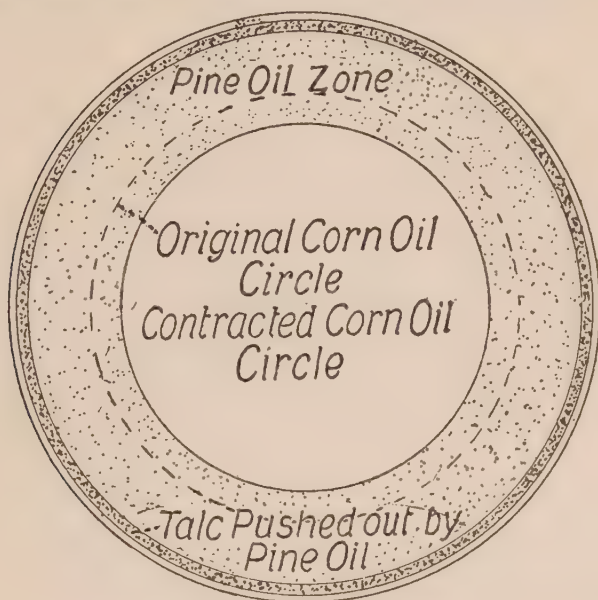


Figure 1.—Illustrating the behaviour of a very thin film of corn oil.

open net-work, the area could be reduced but not expanded without breaking the filaments; but if the oil existed as a continuous film, the area could neither be reduced nor expanded. Any attempt to reduce the area was observed to produce an effect similar to that in the first stages of an ice jam; and any attempt to increase the area always produced a straight clear fracture exactly like that of a broken pane of glass, showing that the film had become a very brittle solid.

The force required to produce this fracture increased with the thickness of the film formed through the addition of the permanganate of potash.

To fracture this solid film, it was first sprinkled lightly with talc, whose particles were observed to be stationary, and then a small (microscopic) particle of corn oil, an oil which always disintegrates into microglobules, was deposited at the centre of the area. Immediately three straight fissures began to radiate from the corn oil droplet, inclined to each



Figure 2.—The contour of the corn oil circle with a thicker film of corn oil.

other at 120° , and soon extended to the circumference, thus splitting the film into three equal sectors. Through these channels the corn oil was observed to flow rapidly, where, if the quantity was not too great, it was afterwards found as microglobules floating on the water between the solid banks.

If the pine oil, however, was not sufficiently thick to form a continuous film, and a particle of corn oil was deposited in

the centre of the area, the following varieties occurred in the action:

(a) If the average thickness of the pine oil was very small, the corn oil cleared off a circle with a very sharply defined contour, and after the first sudden invasion the area slowly contracted into a smaller space. This is represented in Fig. 1. If pure water or water coloured with methyl violet was used, the area cleared by the corn oil was always after this pattern, though when thick it did not contract.

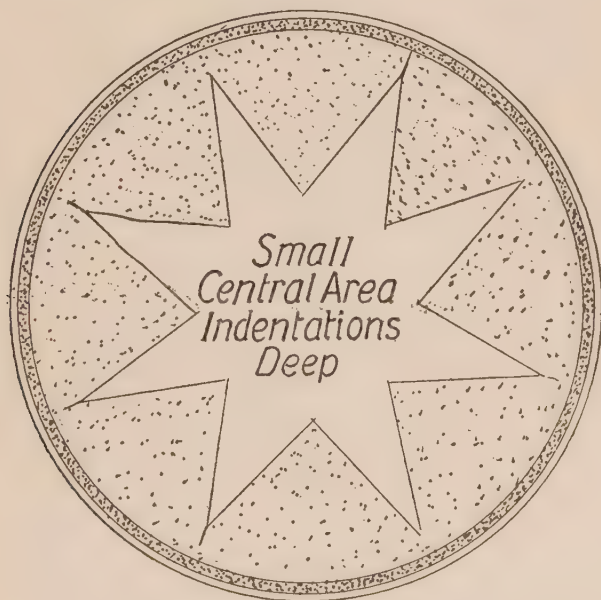


Figure 3.—Phenomena with still thicker corn oil film.

(b) With increasing thickness of the pine oil the contour of the corn oil circle became dog-toothed or indented as represented in Fig. 2.

(c) As the thickness still increased, the corn oil area decreased in extent, the dog-toothed projections became fewer and larger and the indentations deeper towards the circumference of the vessel. This is shown in Fig. 3.

(d) Then star-shaped openings with smaller central area appeared having a tendency to fracture the surrounding area radially at the points into triangular masses having the properties of a film of solid, as in Fig. 4.

(e) With one kind of pine oil, the first one or two droplets of corn oil cleared off a circular area having a clear contour as in Fig. 1. Afterwards additional droplets of corn oil fractured the surrounding zone radially into four-sided figures as in Fig. 5.



Figure 4.—A later stage of a thick film.

(f) When a certain thickness of the film was reached, differing with different grades of oil, a small droplet of corn oil deposited at the centre remained for a moment intact; and then broke the whole surface into three triangular pieces as described previously. This is shown in Fig. 6.

The following two tables show the results of testing the effectiveness of two kinds of oil used in the Coniagas Mines at Cobalt. The first is called "Pine Oil No. 350", and the

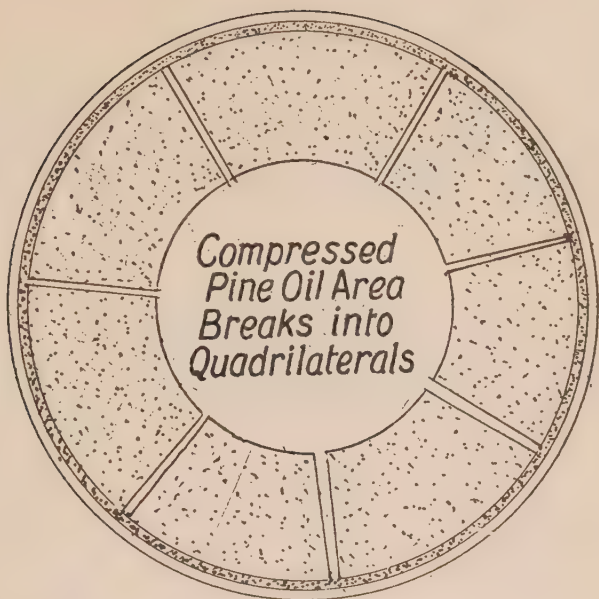


Figure 5.—Illustrating the behaviour of another kind of pine oil.

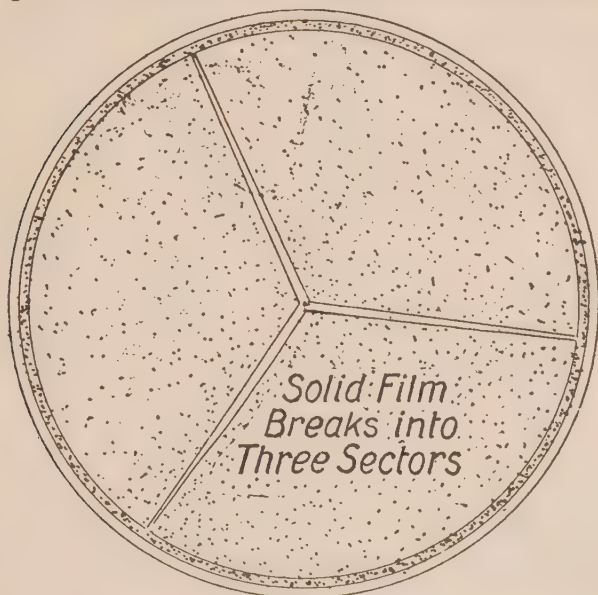


Figure 6.—Pattern obtained with a certain thickness of corn oil film.

other is a mixture invented by Mr. Reid, the manager of the plant, and will be designated as "Mixture No. 4". The strength of the solution of permanganate of potash was 1 to 2,000 parts by weight in water.

TABLE I
"PINE OIL No. 350."

	Vol. of oil droplet in 10^{-6} c.c. units	Area cleared by the spread- ing in sq. cm.	Av. thickness of oil in mol. diams.	Character of the oil film
1	.557	28.3	.25	Fig. 1
2	1.77	38.5	.58	"
	Contracted to	26.4	.84	"
3	5.21	63.6	1.02	"
	Contracted to	56.7	1.15	"
4	8.83	63.6	1.74	"
5	25.8	69.4	4.65	"
6	26.2	70.9	4.73	" with 3 suc- cessive expansions
7	39.4	69.4	7.10	Fig. 2
8	39.2	70.9	6.90	Fig. 5
9	54.2	70.9	9.55	"
10	60.0	70.9	10.6	"
11	79.5	70.9	14.0	" central circle 1 cm. in diameter
12	152	123	15.3	"
13	161	121	15.1	"
14	90.6	70.9	16.1	Fig. 6
15	103	69.4	18.5	"
16	148	70.9	26.1	"
17	536	394	49	"
18	306	432	54	"

In most cases from Nos. 8 to 13 inclusive, the surrounding zone, into which the pine oil had been compressed by the spreading of the corn oil in the central area, exhibited the properties of a film of solid.

There is, then, a clearly defined limit to the thickness of

the film, below which the film is discontinuous, having undergone disintegration, and above which it is continuous, being unable to disintegrate. For this pine oil this limit is between 15 and 16 molecular diameters.

TABLE II
"MIXTURE No. 4"

	Vol. of Droplet in 10^{-6} c.c. units	Area of Spreading in sq. cm.	Average thickness in mol. diams.	Character of the oil film
1	1.69	28.3	.75	
	Contracted to	15.9	1.33	Fig. 1
2	3.36	56.7	.84	
	Contracted to	28.3	1.48	Fig. 2. Small indentations
3	1.04	12.6	1.03	
	Contracted in a deformed area			
4	.37	3.14	1.46	Fig. 1.
	Contracted to	1.77	2.59	
5	10.14	66.5	1.91	Fig. 2.
	Contracted to	44.2	2.68	"
6	10.14	50.3	2.54	"
	Contracted to	19.6	6.50	"
7	19.8	69.4	3.60	Fig. 3.
	Contracted to	38.5	6.40	" Deep indentations
8	22.4	69.4	4.40	"
	Contracted to	44.2	6.3	"
9	26.2	69.4	4.7	"
	Contracted to	55.4	5.9	" Small central area
10	32.8	70.9	4.2	Fig. 4.
	Contracted to	52.8	5.6	" Star points extend far out
11	32.8	70.9	5.8	" No contraction
12	47.8	70.9	8.4	Fig. 6.
13	56.4	70.9	9.94	"
14	57.7	70.9	10.2	"
15	58.9	70.9	10.4	"
16	190	70.9	34	" Narrow straight fissures

In most cases up to No. 11, as in Table I, the compressed surrounding zone exhibited the properties of a solid film which

became more pronounced as the thickness increased. Here the thickness of the film at which the film ceases to disintegrate and becomes continuous is between 6 and 8 molecular diameters.

The wall structure of the froth appears then to depend on this property of the pine oils to form, next to any air surface, a thin strong elastic film that will not disintegrate as all the other oil films do. The fact that "Mixture No. 4" forms this film at about half the thickness of that in the case of "Pine Oil No. 350", indicates that, other properties being the same, the former would be more economical in use than the latter, since the same quantity of oil would form about double the area of structural film.

ARTICLE XII

THE TRANSMISSION OF ENERGY BY THE WATER MOLECULE.¹

It was suggested to the writer that something further might be contributed to the questions so interestingly discussed by Professor R. W. Boyle in his paper on "Rain-making" in the May number of *The Engineering Journal*. Professor Boyle need not offer any apology for introducing "the physics of a very common and ordinary phenomenon" but the writer will go further by saying that some phenomena are so common and ordinary as hitherto to have escaped any critical examination at all. This is especially true of some phenomena to which the writer wishes to call attention in the hope of closing one of the wide gaps that still exist in our knowledge of the world about us.

One of the key problems introduced by Professor Boyle is that of the latent heat of condensation. We know the exact amount of this heat energy; we know that it disappears when water is turned into steam, that it reappears in exactly the same amount when steam is condensed into water, and that the temperature remains constant at 100°C. during these changes. But we do not know the form or the exact location of this energy while it is hidden or "latent" in the steam. The solution of this question would very probably throw light on some others of great practical importance such as those related to the production of the vast fields and forests of Canada.

To fix our ideas, let us think of a cubic centimetre of water. Its mass is one gram. When it is turned into steam at air pressure it occupies 1,700 c.c. In that form it consists of thirty-four thousand billion billion molecules separated

¹Reprinted from "The Engineering Journal", July and September 1922.

from one another. Each is a tense, hard, but elastic sphere having a diameter of 0.0000000385 cm. and the mean distance between them is about twelve times this diameter. Each has its own random velocity which is uninfluenced by the others except when the molecules happen to come into contact with each other and with the sides of the containing vessel. We know that these molecules in this separated condition contain 498 calories of heat energy which they did not contain when as water they occupied only one cubic centimetre at the same temperature. So long as the molecules are in this separated condition this large quantity of energy cannot by any known means be detected, although its amount is sufficient to raise the temperature of five times the quantity of water from the freezing to the boiling point.

Many attempts have been made to trace this energy to its source. The fact that the steam engine is able to do work only after this enormous amount of latent heat energy has first been expended shows how important is the question. Unless this energy is recovered as heat which can be used at temperatures below 100° C. it is a total loss economically. But steam engines and steam heating plants still continue to distribute heat by mysteriously hiding it away on its journey. Various speculations, or hypotheses as they are called, regarding the nature of this energy have been put forward but all to little purpose. One of these hypotheses is that of molecular attraction, by which two molecules when close together are thought of as pulling each toward the other just as the earth and the moon attract each other by gravitation, but with a much stronger force. This force, however, ceases to pull at all when the molecules are more than two or three diameters apart. In steam, therefore, the molecules are too far apart for them to attract each other except when they are near collisions. Another and more modern hypothesis conceives of two molecules as both pulling and pushing each other simultaneously with two forces which depend by different laws on the distance the molecules are apart. Now while these two hypotheses may tell us the way in which two molecules may be held together in water, they do not tell

us how the molecules of steam hold the latent heat energy. It was thought also that these hypotheses showed how the surfaces of all liquids are endowed with that tension which we know pulls against itself at all points and in all directions in that surface, but these explanations are not now seriously entertained although they are in all text books which deal with surface tension.

The writer proposes to show how these two problems concerning the latent heat of steam and the nature of surface tension were both solved by a single method, which disclosed as well, how the sun's energy is held in the atmosphere and transmitted to the different parts of the earth's surface.

As in the surface of water in a vessel so in the surface of a rain drop there is this tension or force pulling against itself to lessen the extent of that surface. On each side of a line 1 cm. long it pulls with a force of 73.3 dynes. (1,000,000 dynes is the air pressure on a square centimetre.) In consequence of this tension each square centimetre of water possesses 73.3 ergs of potential surface energy (41,840,000, or J ergs is one calorie, which is the energy required to raise one gram of water through 1° C.). Now, since long before the first shower wet the skin of primitive man, water drops have coalesced whenever they came into contact, and large ones have broken into smaller ones whenever the sea dashed itself against the rocks. Suppose, then, that three rain drops, 0.3, 0.4, and 0.5 cm. respectively in diameter, come into contact and coalesce. The resulting sphere will have a diameter of 0.6 cm. By this act the total surface has been reduced by 0.44 sq. cm. Consequently, the potential surface energy has been reduced by 0.44×73.3 or 32.3 ergs. This energy is now in the form of heat and the water will be so much warmer, (0.000068° C.). If the temperature remains constant, the heat will be available for other purposes. On the other hand it will require exactly this amount of energy to break up the large sphere into the three smaller ones again, and the energy will then be properly called the latent heat of the three spheres. This simple piece of reasoning suggests that latent heat is simply surface energy which has

to be supplied whenever the free surface enveloping mass is increased and which reappears whenever that surface is decreased in extent.

The writer published the general case of the reasoning given above in the *Philosophical Magazine*,¹ and it may be well to give here a brief outline of its main features.

The amount of potential service energy changed into heat when N drops of water each having a diameter of d cm. coalesce into one mass is proved to be

$$T \left(\frac{36\pi m^2}{\rho^2} \right)^{\frac{1}{3}} N^{\frac{1}{3}} \text{ ergs,}$$

where m is the molecular weight of the substance, ρ its density, and T its surface tension. If L is the latent heat in calories of one gram mass of the substance, the total latent heat of m grams is mLJ ergs. When these two amounts of energy are put equal and the resulting equation solved, we obtain

$$N = \left(\frac{(LJ)}{T} \right)^3 \frac{m\rho^2}{36\pi}.$$

Now it has been proved experimentally that the surface tension of a liquid increases by the same amount for each degree that the temperature is lowered. It will, therefore, have its maximum value at -273°C. even though the liquid has become a solid. The reason that surface tension increases with lowering temperature is that the molecules in the liquid lose in velocity as the temperature goes down. At -273°C. the molecules are at rest and the tension is that of the molecule itself. For water the molecular tension is 133.6 dynes per cm. Also after allowing for the work of pushing the air back to make room for the steam there remains 498 calories of energy which is the true latent heat of a gram mass of steam. Moreover, the molecules of water at 4°C. may be supposed to fill up all the space so that the molecular density may be taken equal to 1. When these values are substituted in the above equation we obtain, $N = 6.05 \times 10^{23}$. This is the exact number of molecules which is known to be in 18

¹Vide Article I, p. 24.

grams of water. It is the same for m grams of any substance and is known as Avogadro's number. While the existence of this number was discovered more than a century ago its actual value has only recently been determined. By using a method totally different from the one described above Millikan obtained the value 6.065×10^{23} ; Perrin, likewise, by another method, obtained a somewhat larger value. Now the writer also found that in the case of nine other liquids the method of coalescence gave results of the same order of magnitude as water. It is difficult then to escape the conviction that the law of coalescence, which never fails to act for all visible liquid spheres, is effective down to the last two molecules. *

From this there seems to be no alternative but to regard the latent heat of steam as the potential surface energy of the free molecules of which the steam is composed. Few laws in the physical world rest upon so solid a foundation. It necessarily follows (1) that free molecules possess surface tension which is somewhat greater than that of the liquid into which they condense, (2) that each free molecule carries a definite amount of potential surface energy equal to mLJ/N ergs which it cannot give up so long as it does not touch another, and (3) that when free molecules suffer an impact they do not rebound like rubber balls but attach themselves to each other by means of their surface forces which, on account of their relative velocity being too great, allows them to separate again with their total kinetic energy unchanged.

This law may be further illustrated. In 18 grams of liquid water which is composed of six hundred thousand billion billion molecules there are only 33 sq. cm. of exterior surface. To convert this water into steam will require 8,978 calories of energy. The separated molecules will then have a total surface area of 69.7 acres and will be loaded with precisely 8,978 calories of potential surface energy. Now, we may suppose that when these molecules coalesce they go, at first, into groups of two; secondly, the groups of two into groups of four; thirdly, the groups of four into groups of eight; and so on. This process of pairing would occur 79 times, not more, before

the steam would become a single mass of water. The changes in surface area and in potential surface energy are given in the table below.

Order of pairing	Reduction of Surface in acres	P.S.E. changed to heat, in calories
1.....	14.5	1847
2.....	11.5	1466
3.....	9.11.....	1163
4.....	7.23.....	934
5.....	5.76.....	733
6.....	4.56.....	582
7.....	3.62.....	462
8.....	2.88.....	366
9.....	2.28.....	291
10.....	1.81.....	277
<hr/>		
Total for first 10 orders.....	63.25.....	8121
Bal. for rem. 69 orders.....	6.45.....	857
<hr/>		
Total for complete cond'n.....	69.70	8978

Again, to use Professor Boyle's illustration, the heat produced in 1000 cu. ft. of air containing 420,000,000 fog particles, which condense into 1/150th ounce of water, amounts to 9,500 ergs; but the heat produced in forming the fog particles from the molecules amounts to nearly 3,930,000,000 ergs, or 48 calories.

We may now understand the process by which nature not only irrigates the land surface of the earth, but transmits the radiant energy of the sun through the envelope of air. The energy of the sun's rays, intercepted by all surfaces containing moisture and all water surfaces, is employed to create free surface areas about the molecules in which it is stored as potential surface energy. The way the molecules are separated from the liquid is similar to the way a water drop is broken away from a larger mass. When free they move away with their kinetic energy undiminished in longer free paths, notwithstanding that each now carries a load of potential energy nearly twelve times as great as its own kinetic energy. In the upper regions of the air, after various encounters with dust particles, molecules of air, and each

other, the water molecules go through the first stages of their condensation during which, as we see from the table previously given, large quantities of latent heat which they carry as potential surface energy are released and become effective in raising the temperature of the air. Thus, if the condensation proceeds through the tenth stage and halts, the moisture in the air will consist of small spherical particles each containing 1,024 molecules and having a diameter ten times that of a molecule, but they will still be too minute to be seen with a microscope. The heat produced, however, will be as great as 90 per cent. of the whole latent heat and will be sufficient to raise the temperature of the air by a sensible amount.

This distribution of the radiant energy of the sun by the water molecules carrying it as potential surface energy and releasing it to warm the air by the simple process of coalescing may be further illustrated. A garden plot in the Niagara Peninsula, thirty by forty feet, has a rain-fall of about thirty inches. To set free the necessary number of molecules and load them with their potential surface energy the sun must supply power equivalent to that of an engine of 1,500 horsepower, running continuously throughout the year. Not only is the water furnished to enable the plants to feed and grow but the heat that "keeps up the steam" is all employed to warm the air that the plants may breathe. To produce a British Columbia fir tree the same powerful engine must work continuously for 200 years.

This is nature's means of making effective her plan of storing the sun's energy in large amounts on the earth's surface in a more or less permanent form. It enables her to maintain the water elevations as a constant source of energy which, for the first time, we are now using in large amounts. It brings about the necessary conditions of moisture and temperature to enable the direct sunlight to produce by chemical action the various hydrocarbons upon which our life depends. Indeed, but for this the extremes of temperature during the day and night would be so great as to render life of any kind impossible.

There is no doubt that the large quantities of heat yielded up by the water molecules in the air during the early stages of their coalescence, or condensation, is a considerable factor in causing storms of various types. A large column of warm air, hundreds of miles in diameter, is gradually formed over a certain tract of the sea or land. This air, being lighter, begins to be replaced by colder and heavier air masses from the outside thus causing surface winds towards a common centre. The motion of the earth on its axis together with the inclination of the earth's surface to the axis then diverts this central direction of the winds into a wide circular sweep so frequently recorded in the weather charts of America. The warm central water-charged column of air spreads over the colder layer beneath and the invisible water spheres coalesce into visible particles between these layers where they are seen as clouds, and on further coalescence fall to the earth as rain. In all this process the remaining part of the latent heat or potential surface energy is released to warm the colder stratum of air beneath, until a state of equalized temperature and saturation is attained, marked by clearing skies and falling winds. In some cases the concentration of these phenomena in small areas results in violent cyclonic storms. In most cases, however, the great heat produced during the first stages of molecular condensation results in the formation of stratified layers of air of different temperatures containing water particles of unequal sizes. These particles condense, as before, between the strata and tend to form clouds, thus equalizing the temperatures of adjacent layers; while, according to the degree of saturation, either the visible particles coalesce further into rain or the clouds disappear altogether.

Again, in some unexplained way we know that the particles of water in a cloud or stratum of air become charged electrically, not improbably by the addition or removal of electrons which are held in, and by, this force-surface enveloping the spheres and from which they cannot escape. If two such charged particles happen to coalesce, the electrons in them instantaneously make a new adjustment on a con-

tracted superficial area. This causes the density of the charge (the number of electrons per unit of area), to be altered, that is, the charge is held at a different potential. Now the water particles which come from the same part of the earth's surface carry like charges and, consequently, any coalescence that takes place causes an increase in potential. The mutual repulsion between these similarly charged particles no doubt delays the coalescence by hindering contact, or perhaps in some case prevents it altogether. This may be the cause of the particles of water remaining in a cloud or fog in a stationary state of condensation. Notwithstanding this, the condensation is considerable and the charge on the particles of a cloud or invisible stratum is raised to a high potential difference from the surrounding air. When such a cloud or stratum meets another having an opposite charge, there is a passage of electricity from the one to the other. At the same time the water particles of the one are attracted to those of the other and coalescence is greatly augmented, attended by the release of heat and increased precipitation of water. This is given as an explanation of thunder storms.

Not only human life, but life of all kinds, animal and vegetable, depends on the fact that energy which comes from the sun by radiation is held on the surface of the earth in some potential form for a longer or shorter time. The only way we know now of replenishing this store of potential energy is by the production of the various hydrocarbons of which our food, clothing, and, in great part, our shelter consists. Nature is doing this on a prodigious scale, but probably not at so great a rate as in the carboniferous age. The capture of the sun's radiant energy and its distribution by the water molecules is an essential part of the process. But for this, the heat rays from the sun would pass through the air without raising its temperature. Without the water molecules to carry the heat away, the solid surface of the earth would become extremely hot during the day by the absorption of large quantities of heat and would cool off during the night, when all this heat would be radiated into space again. The

practical application of the solution of these problems lies in a fuller knowledge of the laws by which nature is working, so that we may enable her to increase her output. The possibilities in this direction are almost unlimited.

To sum up: the water molecule on escaping from its liquid assumes a load of potential energy on its surface exactly equivalent to the energy of its dissociation supplied by the sun's rays. It carries this energy through the air unchanged in amount, whether its own motion be slow or swift. Through the act of coalescence on contact with other molecules in the air, both this energy as heat and its mass as water are made available at various places on the earth's surface. These then, through the action of the direct rays of sunlight in the presence of living organism, are instrumental in producing the various hydrocarbons of which the stores of the earth's potential energy consist.

ARTICLE XIII

THE ORIGIN OF THE ROTATION OF THE PLANETS

The motions of the planets in the solar system are almost fully accounted for by the classical mechanics of Newton, in which gravitation is the controlling force. More recent investigations, however, in the realm of astrophysics have opened up the question as to whether the forces brought into play by the existence of great magnetic and electric fields in space are in reality the cause of many unexplained astronomical facts. But it still remains in doubt whether the system of the universe, even with the aid of the Einstein equations to express the most general physical conceptions, can be satisfactorily explained in terms of either or both of these forces.

Yet the existence of these facts constitutes a most alluring challenge to the scientific mind to attempt their solution. To mention only a few of these unsolved problems is to show how little is the progress that has been made. How does the sun maintain a constant temperature while radiating such enormous quantities of energy? How does radiant energy originate, propagate itself through space, and terminate its existence? What is the nature of interstellar space and of the structure and properties of ultimate matter? No one would now venture to say that the old problems in molecular physics concerning the nature of surface tension and the source of the latent heat of condensation have nothing to do with the sun's radiation or the motions of the heavenly bodies.

In Fig. 1 are shown the processes by which two liquid spheres coalesce into one and are separated again. These phenomena have always been explained by the action of surface tension which tends to diminish the enveloping area about masses. It will be observed that the two drops retain their perfect spherical form until contact actually occurs and then the process of coalescence begins suddenly and after a series of interesting changes ceases gradually

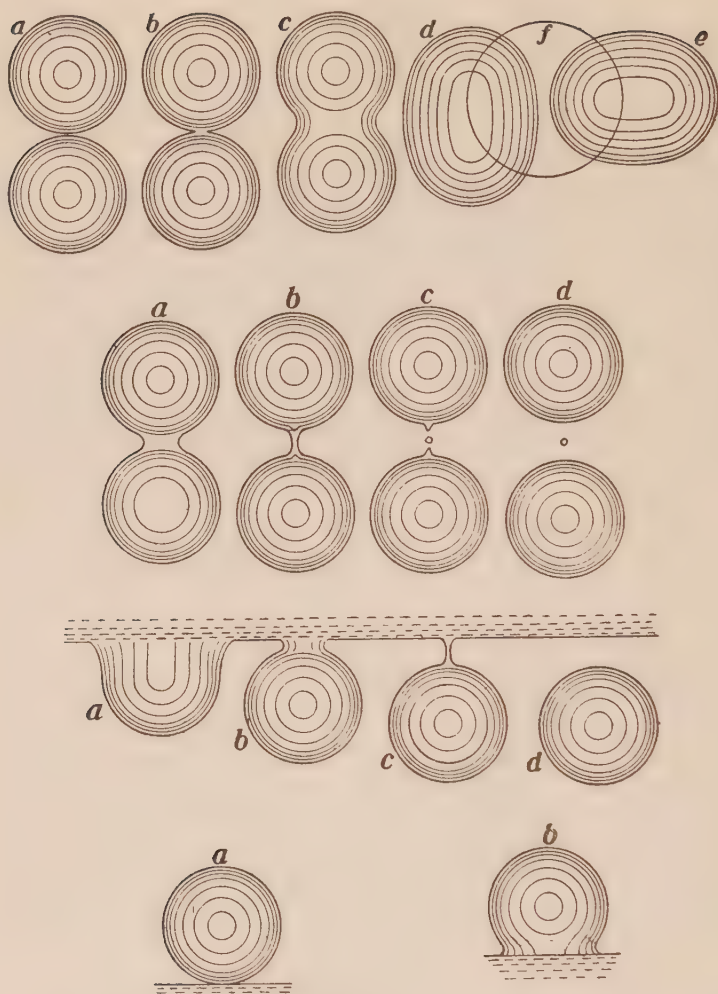


Figure 1

when the two drops are united into one sphere. On the other hand, when a drop is separated from another or from a large mass, a connecting neck of water is formed, gradually decreasing in diameter to a narrow cylinder which is pinched apart and the projections pressed in before the parts assume their perfect spherical form. The two processes are not re-

versible, though their final and initial states may be. In the first the process does not begin until the distance between the centres becomes equal to the sum of the radii, in the latter it does not end until this distance greatly exceeds the sum of their radii.

It occurred to me to investigate the change in the potential surface energy involved in the process, and the results of the original investigation were published in the number of the *Philosophical Magazine* for June, 1921. The following summary of this investigation will assist in making clear the present paper.

The potential surface energy which is changed into heat when three water drops 3, 4, and 5 mm., respectively, in diameter coalesce into one was found to be 7.71×10^{-7} calories, and generally the potential surface energy appearing as heat when n drops of diameter d coalesce into one mass is

$$\frac{T}{J} \left(\frac{36m^2\pi}{\rho^2} \right)^{\frac{1}{3}} \cdot n^{\frac{1}{3}} \text{ calories.}$$

This amount of heat was produced solely by the decrease in surface area of the spheres. In seeking to verify this reasoning, use was made of the fact that one gram molecule (m grams) of water required mL calories of heat to vaporize it into steam at the same temperature. Putting these equal, we had the equation,

$$\frac{T}{J} \left(\frac{36m^2\pi}{\rho^2} \right)^{\frac{1}{3}} \cdot n^{\frac{1}{3}} = mL$$

from which

$$n = \left(\frac{LJ}{T} \right)^3 \times \frac{m\rho^2}{36\pi}$$

where L , J , T , and ρ were already very accurately determined. On making the calculations n turned out to be

$$6.05 \times 10^{23},$$

which is within 1/3 of 1% of Millikan's determination of the number of molecules in a gram molecule of any substance. Nine other substances gave results of the same order of magnitude. No others had the necessary data determined.

The importance of this result at once became evident.

It connected the invisible phenomena of the molecular world with the visible phenomena constantly happening all about us, and brought them all under one simple law. It indicated that some of our fundamental conceptions might need revision.

(1) The process of condensation consists of repetitions of the act of coalescence, beginning with the free molecules of the gas and ending when all the molecules are gathered into one liquid mass.

(2) Each free molecule of a gas must then possess as its inseparable property a force enveloping its mass tending to decrease its exterior area, that is, the free molecule possesses surface tension. It is, therefore, a perfect sphere, tense and elastic; but its elasticity is due solely to the action of the surface force and the absence of any internal force, and not to the action of internal forces and the absence of surface tension.

(3) The free molecule must also be conceived of as carrying a definite amount of potential surface energy equivalent to mLJ/N or $\pi d^2 T$ ergs.

(4) Instead of its size being estimated by "the radius of impact", the free molecule has a definite diameter, such that

$$d = \left(\frac{mLJ}{\pi TN} \right)^{\frac{1}{2}}.$$

(5) It is no longer possible to explain surface tension on Laplace's hypothesis of the attraction of molecules, since the force acts about the free molecule itself when no others are within the range of its attraction.

This brings up the question of the subsequent behaviour of two spheres if they should come into contact and coalesce while each is moving in its own free path with its own momentum—a condition of affairs that actually exists. The problem of the impact of two elastic spheres which are free to bound apart again has been solved, but that of two coalescing spheres has, as far as I know, not been dealt with, and the following is an attempt at a solution of the simplest case only.

Suppose two liquid spheres of radii r , with equal and

opposite velocities v , move with their centres along two parallel lines whose distance apart is $2r$. Then their common centre of gravity coincides with their contact-point and is at rest. Contact occurs with a resultant pull of the surface forces along the revolving line of centres. Since the spheres are drawn into one whose centre is the stationary common centre of gravity, there can be no linear motion. The resulting sphere, therefore, will revolve about a fixed axis perpendicular to the plane containing the parallel lines.

If ω be the angular velocity of the line of centres about the axis at the instant of contact when coalescence begins, then the moment of momentum, or angular momentum, about the fixed axis through the common centre of gravity

$$= 2.M.v.r \text{ or } 2M.r^2.\omega, \text{ since } v=r\omega,$$

where M is the mass of each sphere.

After the coalescence is completed, if it be assumed that the whole mass moves as though it were a solid, the radius of the revolving sphere is $2^{\frac{1}{2}}.r$ and it moves as though its mass were concentrated at a distance from the axis equal to the radius of gyration of the sphere, which is equal to $(2/5)^{\frac{1}{2}}.2^{\frac{1}{2}}.r$. If this be denoted by r' and the linear velocity of the concentrated mass be v' and the angular velocity be ω' , then the angular momentum

$$2.M.v'.r' = 2.M.r^2.\omega' = 2.M.(2/5).2^{\frac{3}{2}}.r^2.\omega'.$$

Since no change can take place in the angular momentum of a body through any interaction of its parts, these two expressions for the angular momentum are equal, that is,

$$2.M.(2/5).2^{\frac{3}{2}}.r^2.\omega' = 2.M.r^2.\omega$$

whence $\omega' = (5/2^{\frac{3}{2}}).\omega = 1.555.\omega$.

The linear velocity of a point on the equator of the sphere

$$= 2^{\frac{1}{2}}.r.\omega' = (5/2^{\frac{1}{2}}).v = 1.982.v.$$

The linear velocity of the extremity of the radius of gyration

$$= (2/5)^{\frac{1}{2}}..2^{\frac{1}{2}}.r.(5/2^{\frac{3}{2}}).\omega = 5^{\frac{1}{2}}/2^{\frac{5}{2}}.v = 1.25v.$$

If, however, a velocity v parallel to the direction of their motion be given to each sphere, one of the spheres will have

a velocity of $2v$ and the other will be at rest, while their common centre of gravity will have a velocity of v . In addition then to its rotation about an axis, the resulting sphere will have a velocity of translation of v .

It is possible to determine the resulting motions of two spheres impinging on each other and coalescing under more general conditions, but this must be postponed for the present.

To test out a simple case, a glass plate covered evenly on one side with smooth paper was fitted in a board and made horizontal. A raised border prevented mercury spheres from rolling off either the glass or the paper surface according to which was uppermost. With the glass surface the adhesion between mercury and glass was so great that a mercury sphere could be put in any desired position, but it hindered the free motion of the sphere. On the other hand the adhesion of the mercury to the paper was so small that it was difficult to control the position of the sphere. To obviate this a small circular opening was made through the paper in the required position which enabled the mercury sphere to adhere to a small area of the glass when brought above the opening.

Now had there been no spots on the sun we should probably never have found out that the sun rotated on its axis once in about 24 days 7 hours in the same direction as the planets revolved. We cannot observe the rotation of rain drops because there are no spots on them by which the side shift may be seen. It is essential, then, that the mercury sphere on the plate have a few particles of dust on its surface. These will soon settle on the plate from the air and will attach themselves to the sphere as it rolls over the plate and may be seen with a magnifying glass. The sphere cannot be set in rotation by a side blow with any sharp or rough instrument as a billiard ball can be, nor can its rotation be retarded by the same means. Change in its rotation can be effected only by shooting along its side a stream of molecular or larger particles which coalesce with it or adhere to it for a short time and then fly off. Thus a small stream of air directed along its side will set the sphere spinning in a very interesting way. If, however, the sphere be left exposed to the air for a few hours, a

rigid crust is formed on its surface which prevents the stream of air from giving it a rotation; but a small rotating glass sphere will, on touching its side, cause it to turn as though the two spheres were cogged together. Such a sphere, if it were free in space, would be a close model of our earth.

In attempting to exhibit this effect experimentally a mercury sphere was placed in position and examined (with a magnifying glass) to see that it had no rotation. Another one, of about the same size, was then projected horizontally from a small glass tube by means of a piston operated by a miniature catapult machine. The spheres are shown in Fig. 2. The direction was so adjusted that the projected sphere would just make contact with the other. At the instant of contact neither sphere was rotating; but immediately afterwards the coalescing force joined them together and a series of evolutions took place, resembling at one period the motions of a dumb-bell whirled in the air, which resulted in the two masses forming one spherical mass apparently at rest in some fixed position on the glass or paper. On looking at it with the magnifying glass, however, it was observed to be in rapid rotation about a vertical axis. The rotation continued for 20 or 30 seconds and longer if the sphere rested on the paper surface. It would appear that the angular momentum of the separate spheres at the beginning of the coalescence was gradually changed into the angular momentum of the combined spherical mass revolving as a solid about an axis. If the spheres had been free in air when this took place, the resulting rotation would continue till the angular momentum was all imparted to the air molecules attaching themselves to the surface for a time. If this took place in free space the resulting rotation would continue forever.

Secondly, when the projected sphere was given a greater velocity, the process of coalescence proceeded only to a certain stage, when, on account of the centrifugal forces being too great, the connected masses separated again and took up fixed positions on the plane. When these spheres were examined as before, they were found to be revolving rapidly in the same direction as the original line of centres. If, as



Figure 2

before, we imagine this to take place in free space, the resulting motions would be perpetual. The spheres would also possess linear motions depending on the conditions of impact.

Thirdly, by still further increasing the velocity of the projected sphere and inclining its direction slightly towards the other, the two original spheres were afterwards found as three or more separate spheres of various sizes all revolving in the same direction, though on one or two occasions I thought one small sphere had a rotation in the opposite direction.

Lastly, in a head-on collision the projected sphere appeared to coalesce with the other on the one side, to pass through it, and to separate again with an increased or di-

minished mass on the opposite side leaving sometimes one or more smaller spheres along the line of the motion. In this case no marked rotation of the spheres was noticed.

It appears, then, that when two free liquid spheres, on coming into collision while possessing only linear velocities, either combine into one sphere possessing both linear and rotational motions or separate into two or more spheres each of which possesses both linear and like rotational velocities.

Now there are very convincing reasons in favour of the view and none against it, as far as I know, that what we have observed here in the case of two mercury spheres is precisely what happens in the case of individual molecules in ether space. If this be granted, and we can imagine a vast three-dimensional region to contain enough molecules to constitute the mass of the solar system, and by the radiation of heat energy to slow down the velocities of these molecules, they will at length coalesce in the way we have seen into a number of separate liquid spheres each moving in a line and possessing its own rotation. There comes a time, however, when the spheres reach such a size that their gravitational attraction for each other becomes great enough to be compared with the force which causes the coalescence of the spheres and holds them in their spherical form. The diameters of the spheres when this condition obtains may be found as follows:

Let d be the diameter of the sphere, ρ the density of the liquid, T its surface tension, and G the gravitational constant which is equal to 6.658×10^{-8} .

Then the total force exerted by the enveloping surface tension on opposite sides of an equatorial line to hold the mass together

$$= \pi d T.$$

(a) If the sphere be regarded as composed of two solid hemispheres held together by no other forces whatever except the gravitational attraction of their masses whose centres of mass are at a distance of $3d/8$ apart, the gravitational force holding the masses together

$$= G \left(\frac{\pi}{12} d^3 \rho \right)^2 \bigg/ \left(\frac{3d}{8} \right)^2 = 4G\pi^2 d^4 \rho^2 / 81.$$

If these are assumed to be equal
then $4G\pi^2 d^4 \rho^2 / 81 = \pi d T$,

from which $d = \left(\frac{81 T}{4\pi G \rho^2} \right)^{\frac{1}{3}}.$

(b) If the sphere be regarded as composed of two spheres which have coalesced, the gravitational force attracting their masses just as the coalescence begins

$$= G \left(\frac{\pi}{12} d^3 \rho \right)^2 \bigg/ \left(\frac{d}{2^{\frac{1}{3}}} \right)^2 = G\pi^2 d^4 \rho^2 / (72 \times 2^{\frac{1}{3}}).$$

Then, as before, $G\pi^2 d^4 \rho^2 / (72 \times 2^{\frac{1}{3}}) = \pi d T$,

from which $d = \left(\frac{72 \times 2^{\frac{1}{3}} T}{\pi G \rho^2} \right)^{\frac{1}{3}}.$

The results are given in the following table:

Substance	Surface Tension	Density	Diameter (hemispheres)	Diameter (two spheres)
Gold.....	612	19.3	5.42 metres	8.93 metres
Mercury.....	547	13.6	6.59 "	10.86 "
Water.....	73.3	1.0	19.07 "	31.46 "
Eth. Alcohol.....	22	.79	10.99 "	18.12 "
Hydrogen.....	8.8	.07	55.8 "	92.0 "

But these forces generally, if not always, act to aid each other, not to oppose each other, and the spheres continue to grow in size till they reach planetary and even solar dimensions by the process of coalescence aided by the action of gravity. The relative effect of these two forces on the surface of the earth in the case of a molecule of mercury entering a liquid mass may be illustrated as follows:

The total pull of the coalescing force

$$= \pi d T = \pi (3.56 \times 10^{-8}) \times 547 = 6.12 \times 10^{-5} \text{ dynes,}$$

$$\text{and its weight} = \frac{200 \times g}{N} = \frac{200 \times 980}{6.05 \times 10^{23}} = 3.17 \times 10^{-19} \text{ dynes.}$$

The coalescing force, therefore, is about 2×10^{14} , or two hundred million million times the earth's attraction upon it.

Again, it may be calculated that a mercury sphere will reach a diameter equal to 12 million million times the sun's diameter before its gravitational attraction for a mercury molecule at its surface will be equal to the coalescing force which pulls the molecule into the liquid.

With respect then to the earth's gravity holding a molecule to the surface as part of a liquid or solid, its effect is infinitesimally small when compared with the coalescing force of surface tension.

On the other hand this latter force has no effect whatever on free masses, molecular or larger, in controlling their individual motions. As soon as a whirling mass of liquid separates into two or more rotating spheres, as it has been shown to do in the experiments described above, each sphere in addition to its rotation moves in its own linear path. This latter motion would, according to Newton's first law, be uniform and rectilineal, were it not that gravitational attraction among the separate masses with a gentle but continual stress holds the spheres in a group, causing each to leave its linear path and revolve in a periodic orbit about the common centre of mass.

In this way it seems possible to conceive how our little solar system may have been evolved from the primary energy of the individual molecules themselves, where the total angular momentum, made up of that due to the rotation of the bodies on their axes and that due to the revolution of the bodies in their orbits about their common centre of mass, is the resultant of the angular momenta of the individual molecules in the space from which the mass of its parts was gathered.

It is just possible that in the light of this illustration the sun's constant temperature may be explained also, but this must be postponed to some future time.

ARTICLE XIV

THE PHYSICAL BASIS OF NUMBER

1. *Introduction.* The processes by which our notions of the fundamental magnitudes of time and space were obtained took place at such an early period of our life, either as an individual or as a race, that our experiences with them are difficult to recall. That these notions resulted from a series of complex experiences there can be no question. The philosopher, however, takes generalized notions as the basis upon which he attempts to build his theory of truth, without enquiring very far into the particular experiences upon which his general notions may be founded. There will always be differences in these general notions depending upon the degree of perfection with which we are conscious of these experiences, or with which we are able to recall them.

Our notion of time, for instance, depends on a conscious experience followed by a connected series of less conscious experiences and ending with another conscious experience. The first and the last of these experiences, distinguished from the others by a greater degree of consciousness, are termed events, while the intervening series of experiences give rise to our notion of the interval which we call time. Whatever that notion may be, it involves the power to recall at least some continuity of the intervening series of experiences. That our notions of time and space are different depends upon the different experiences that form the intervals in the two cases. Thus, our notion of (linear) space depends in part on consciously experiencing, through the eye, two objects, and less consciously, objects between them, involving probably the memory of a previous effort of moving from one object to the other; while the notion of time involves such experiences as continuous pain, the progression of the sun and the gradual fading of the landscape, the acts we will to perform, and the memory of similar experiences.

Probably our first notion was that of an object as distinct from ourselves. Long afterwards we came to recognize that it was only in connection with the objects of our first experiences that these groups of experiences happened by which we obtained the more general notions of space and time.

It is also the less conscious but more extensive series of experiences between two conscious events that constitute the notion that one event succeeds another. If there were no conscious experiences of some kind between two events there could be no notion that one event succeeds another.

2. *Conditions for Investigating the Problem of Number.* However these notions may be obtained, in any analysis which we may make of number there are certain conditions which are essential if we are to be understood. These are:

(a) There must be a general notion of magnitudes as undivided wholes and of their relations and connections with one another.

Thus lines form the boundaries of areas and areas form the boundaries of volumes. Such relations are fundamental in that man has no power to change them. But a line has no connection with time that may be called fundamental in this sense. The two conscious experiences which bound a line series of experiences may happen without any time series of experiences; and the two conscious experiences which bound the time series may occur at precisely the same point-boundary of line-space.

(b) There must be the ability to judge in this general way that one undivided magnitude is greater or less than another undivided magnitude of the same kind.

(c) There must be also the ability to recognize that one event succeeds another.

(d) The words used in defining number must be only those expressing sense perceptions and human action.

(e) The test for the equality of two magnitudes, namely, the bringing of one undivided magnitude into coincidence with the whole or a part of another can be actually accomplished.

Without doubt Euclid's test for the equality of two

magnitudes was based on the actual experience of man, who in fact could cause two lengths, areas, volumes, and even two times to coincide very accurately.

3. *The Fundamental Problem of Construction.* These conditions belong to an early stage in man's development in which progress had been arrested by an obstacle of which he was probably not conscious. When at length the obstacle was overcome, he emerged from caves and lived in dwellings constructed by himself. Euclid referred to this obstruction when he stated his third proposition. In a more general sense the obstruction may be stated in the form of a problem.

Out of an undivided magnitude P' , which was judged to be greater than another undivided magnitude A , it was required to form a new undivided magnitude P , equal to A , where it was impossible to bring A and P' into direct coincidence.

The following account of the solution of the problem may not be historically in order but it presents all the essential elements involved.

4. *The Solution of the Fundamental Problem.*

(1) The first step in the solution was the discovery or selection of a third magnitude U , conveniently much less than A and called the unit magnitude, which could be transferred across the barrier separating A and P' .

(2) The second step consisted in performing a definite series of acts which all individuals by imitation learned to perform. This series of acts was itself a whole composed of four unlike parts, namely, (a) bringing U into coincidence with a part of A ; (b) indicating by markings or by other means the part of A in coincidence with U ; (c) removing U from its coincidence with the part indicated; and (d) separating this part of A from the other part A_1 , that is, removing it from the whole.

(3) The third step was to represent this definite operation. The convenient sign agreed upon was the index finger; later a picture of the finger in the form of a downward stroke; and finally the downward stroke which became the symbol "1" or the word one.

(4) For the final step see Section 8, p. 218.

5. *The Definition of Number.* In the case of continuous magnitudes the symbol "1" then denotes and at the same time defines the whole operation described in section [2] of page 215. If, however, A and P' were groups of objects belonging to a general class of which U was a member, the symbol "1" would only denote and define the part (d) of the whole operation, which is simply the act of dissociating the one object U from the group A . The effect of performing the whole operation section [2], in the case of continuous magnitudes, is to create a new additional object of the general class equal to U . In performing the operation, then, we are only copying on a small scale the act which nature is doing on a large scale in creating new objects which we, from certain resemblances they possess, put into general classes, so that we may call all the members of the same class by a common name. While we have restricted the symbol "1" to refer to the act of detaching a single object from a group of objects, it may still be regarded as denoting as well the other parts of the whole operation by which the object itself was originally created. In any case it is to be observed that the symbol "1" denotes, not the magnitudes A or U , but a definite series of acts which we perform with or upon them; that the series of acts preceded the symbol agreed upon to represent it; and that the definition applies both to continuous magnitudes and to all general classes of objects.

A repetition of this fundamental operation upon A_1 , combined with the first upon A , constituted a definite group of acts which came to be denoted and described by the word or symbol "2". Similarly other definite groups of acts were denoted and described by the arbitrary symbols 3, 4, 5, 6, 7, 8, 9, and the word "ten".

6. *Grouping of the Unit Operation.* A practical difficulty now arose which even the Greek or Roman peoples were hardly able to overcome, namely, of distinguishing higher groups of operations and remembering separate symbols to represent them. The device which finally overcame the difficulty is due to the Hindoo race. It consisted in reversing the order of the unit operations denoted by the word "ten"

as follows:—The equal parts of A , which now constituted a definite group of like objects, were assembled into one whole and the markings obliterated. This whole could now be used as a new unit magnitude precisely as the original unit U was previously used, and the new unit operation described by the same number symbol "1". That this device had been employed was indicated by writing the 1 a letter space to the left of its original position by use of the combination "10", the symbol "0" having no other function than to secure this shift of position.

7. *The Unmeasured Residuum of a Magnitude.* A further and more serious difficulty inevitably arose in the case of continuous magnitudes. With all such, after a certain stage in the operations upon A was reached, there remained a part A_n which was less than the unit U , and the succession of the unit operations could not be continued. The difficulty was partly overcome when a way was found by which the original unit U could be divided into equal parts and these into smaller equal parts. These parts could then be used in further operations upon A_n . It was found, however, that no matter how small was the final unit there still remained a part of A smaller than this unit.

But Euclid does not appear to have noticed this unfailing experience with A and U when he calls such magnitudes incommensurable. If there are commensurable magnitudes, such as he bases his theory of number upon, they were made so by some previous operations of measuring, such as has been described, but their actual existence in the objective world is not known as a generalization of experiences.

If this small inevitable residuum of A , which cannot be entirely eliminated by any conventionalized system of forming small units, be disregarded, the whole actual operation may be denoted and described by a corresponding grouping of symbols which is the number a .

8. *The Final Step in the Solution.* The final step in the solution consisted in taking the unit U across the interval or barrier separating A from P' ; repeating, as described by the number a , the operations upon P' ; reassembling the parts

and obliterating the markings; and finally severing the part P affected by these operations from the other part of P' .

Thus was the problem solved.

9. *Summary and Conclusions of Part I.* If this analysis be true, any number symbol x can have no other function than to describe the procedure by which one magnitude may be constructed out of another. It can tell us nothing of the nature of the magnitude itself or of the properties by which the kinds of magnitudes are distinguished from one another.

The original group of acts represented by the number symbol "1" forms the fundamental unit operation in all conventionalized systems of grouping such unit operations, and each system of grouping will be described by its own conventionalized system of number symbols. The actual performance of this conventionalized group of operations upon any magnitude A and the representation of these operations by a number symbol is known as "measuring" the magnitude A . The whole operation of constructing P equal to A may be performed by different systems of grouping the unit operation and, consequently, represented by different systems of number symbols; but the number a which describes the construction in one system must be capable of being transformed into the number b which describes the construction in another system. The test of the equality of two numbers is that they describe two ways in which the same magnitude P may be constructed from the same unit magnitude U .

The property by which things are classed as magnitudes is that they are capable of being divided into parts which retain the special properties by which the kinds of magnitudes are distinguished, that is to say, they admit of the operations described above without losing their identity.

Antecedent, then, any means of representing them, definite operations had been adopted whereby a magnitude more suitable to human needs could be constructed from another less suitable. The need of conveying information in regard to these operations by means of words and symbols gave rise to the number content of human language. In

course of time both the grouping of the operations and the arrangement of the elementary number symbols became highly conventionalized. But certain psychological tendencies common in the use of language have tended to obscure these fundamental conceptions, until at the present time no generally accepted definition of number can be found.

10. *Mathematical Conceptions of Number.* In pure mathematics number is defined in such a way as to furnish a basis for the development of a consistent system of exact propositions without reference to its actual or historical development. But the sufficiency of this basis lies in the inclusion of at least some physical element in the definition, that is to say, some part of the fundamental unit operation must be involved in the definition.

In particular the theory of functions assumes as a basis a succession of events (points, objects, and happenings) of the most general, that is, of the simplest, nature. The individual events are distinguished, not by their physical properties, but solely by their place in the succession, and are denoted by the ordinal number symbols 1, 2, 3, etc., which are thus defined. The interval between two successive events (or numbers) in this series is, therefore, at the disposal of the mathematician, who at the same time is under the necessity of defining this interval which he may call the property of "betweenness". Counting or measuring then consists of "matching" objects with the events in the assumed succession, (that is, taking them from a general class and putting them into a special class), and giving to the final object (or final matching) the number symbol belonging to the corresponding event. The elementary processes follow and a consistent theory is built up.

But this definition, as is evident, presupposes that the fundamental unit operation had already been performed when the haphazard things or events in a general class were put into the very special ordered class of succession of events. Instead, then, of the number symbol denoting the whole group of unit operations it denotes only the final boundary or completion of the group. The former and more general

definition thus includes the latter and particular definition. Moreover, the series of experiences which constitute our notion of physical magnitude includes the succession of events with the undefined intervals which constitute the mathematical notion of quantity. But, on the other hand, the propositions of pure mathematics are more general in their nature than those in which the intervals are limited to actual physical experiences, since the intervals may be defined in any way.

11. *The Philosophical Conception of Number.* A more philosophical basis for number has been constructed as follows: The haphazard things of the objective world are assumed to be arranged into random groups. Among these, certain groups are found such that the things of one group may be matched, without excess or defect, with the things of another group. Thus all the random groups are composed of classes of groups such that the things in a group of one class cannot be matched, without excess or defect, with the things in a group of another class. These classes of groups are denoted by the number symbols 1, 2, 3, etc., which are thus defined. This notion of number thus appears to be divested of all physical properties and to depend solely on the matching of things or events.

But here, again, this notion involves the fundamental unit operation and its combinations, by which the haphazard things were previously arranged into groups. Instead, then, of a particular number symbol, such as "5", denoting a single group or class of groups of things, it denotes and describes the definite combination of unit operations by which the random group was first formed. The "matching" of two things or events is a part of the fundamental unit operation by which new members of the same class are formed. As before, this definition of number leaves the interval between two successive classes of groups or between two successive numbers undefined.

12. *Special Properties of Space and Time.* The special property of linear space is direction, and our notion of it is a generalization of experiences with various line magnitudes

and of their connections with other magnitudes. With this notion there is associated another of constancy of direction or the property of "straightness". The Euclidian term "evenly between its extreme points", which is considered inadequate as a mathematical definition of straightness, but which Newton accepted in stating his first law of motion, refers to these experiences. The notion of three directions in space such that the motion of a point along any one of these directions can take place without any motion along either of the other two is a generalization of experiences, and is itself a particular experience from which our notion of straightness is derived. The existence of such a set of three directions is assumed in the Cartesian system of coordinates, and constitutes the frame-work of the Einstein equations. Now there can be no notion of absolute position of the origin or of absolute direction of the axes since there are no particular experiences of which such a notion is a generalization. Further, the relative position of a point with reference to the moving origin and whirling axes is determined only by the numbers x , y , and z which only describe the way in which a certain length is made to coincide with other lengths, and no conclusion can be drawn as to the nature of linear space other than that formed by our generalized experiences.

The notion that the physical world is moving from cause to effect by immutable laws involving all things in a continuous progression of events is the special property of time which Newton conceived and described. The time between two events may be measured in the same way as any other physical magnitude where the unit of time is that time during which light travels in vacuo a distance of c centimetres. But the transcendental magnitude conceived of as the one interval between two events in the relativist theory would require a transcendental unit magnitude of the same kind in order to be measured, and neither has yet been defined in terms of experience. Moreover, the prediction or assumption of such a transcendental magnitude in connection with equations whose terms are only descriptions of the operations

of measurement of physical magnitudes is hardly possible unless some other transcendental magnitude or property of space or time is involved previously in the theory.

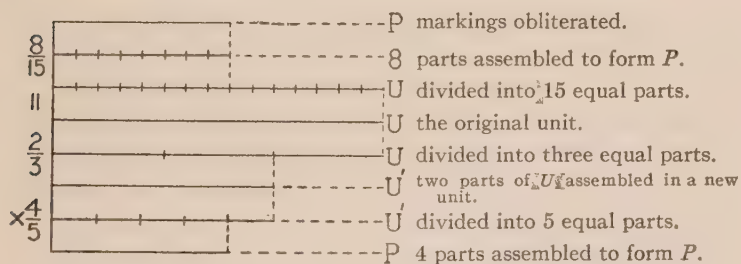
13. *Symbolic Operations with Number Symbols.* Consider the equation

$$a = bc.$$

Here a is a number symbol which describes precisely the conventionalized operation of fitting, by repetition and division, some unit magnitude into coincidence with the magnitude under consideration. Likewise b describes the operation of fitting the same unit magnitude into coincidence with a new unit magnitude, and c describes a similar operation of fitting this new unit into the original magnitude. The equation, therefore, simply states that the original operation of measuring any magnitude is equivalent to two successive operations of measuring the same kind of magnitude. This is the fundamental truth upon which is based the multiplication table and its inverse the division table which for the sake of economy we memorize. Thus the identical equation

$$\frac{8}{15} = \frac{2}{3} \times \frac{4}{5}$$

may be established and explained diagrammatically as follows:



In a similar way may be interpreted every other mathematical identity including those expressing functions in the form of converging series.

14. *Relations of Physical Magnitudes.* But some magnitudes are difficult if not impossible to measure directly. Recourse is then had to the various ways in which they are fundamentally connected with one another. Thus, lines form the boundaries of areas, velocity involves linear space and time, gravitational force acts only on mass, and so on. As time goes on, more and more of these relations are discovered and defined.

In general the simplest relations are the most common.¹ Two magnitudes are frequently found so connected that the same operation of measuring applies to both. Thus, the mass and the weight of a body on the earth's surface are such that one of them cannot be measured without measuring the other. It follows that the numbers representing these operations are identical. This connection, therefore, enables a more difficult operation to be replaced by a less difficult one. Thus, it would be difficult to measure the mass of a body by any direct method if it were wholly disconnected from its weight on the earth's surface; but recognizing this connection we measure the weight directly and use the same number symbol to describe the operation of measuring the mass.

15. *The Principle of Substitution.* This principle of substitution may be further illustrated in the case of the rectangle where straight lines form the boundary. The equation above,

$$a = bc,$$

shows that a , the operation of measuring the area directly, is equivalent to two successive operations of measuring area. But on account of the relations which the bounding lines have to the area of the rectangle we may replace the two latter operations, b and c , of measuring area by the simpler operations, b and c , of measuring lines. These two latter operations may then be transformed by the multiplication table into the single operation a .

Again the same equation,

$$s = vt,$$

applied to a uniformly moving body, shows that the operation,

¹This is Newton's dictum "Nature works in simple laws".

s , of measuring space is equivalent to two successive operations, v and t , of measuring space. But on account of the connection which space has to velocity and time the two latter operations, v and t , of measuring space may be replaced by the equivalent operations of measuring velocity and time. Now it is difficult to measure velocity directly and easy to measure time and space. Then by writing the equation in the form

$$v = \frac{s}{t},$$

we may replace the difficult operation of measuring velocity by the two simpler operations of measuring space and time which may be transformed by division into the single operation.

The symbolic quotient, s/t , or as it is usually written, ds/dt , is simply a number that describes the operation of measuring the velocity, provided that ds and dt are also number symbols. If, however, ds and dt are regarded as unmeasured whole magnitudes, the expression ds/dt has no meaning as a number symbol expressing the measure of a physical magnitude. It would then be simply a word symbol denoting the unmeasured conception of velocity which is obtained on observing a body moving over a distance ds in the time dt and has no element of number concept in it. The equation in number symbols, $v = s/t$, must then be regarded as stating the equivalence of two methods by which the operations of measuring the velocity of a moving body may be performed. It shows how the measurement of velocity may be obtained from the measurements of two other magnitudes, time and space. This is the meaning of a physical law expressed in terms of number symbols as an equation. The form of the equation is determined by the fundamental connection between the physical magnitudes, but in no case may the nature of this connection or the properties of the magnitudes be inferred from the form of the equation.

16. *Physical Laws Expressed by Mathematical Equations.*

A mathematical equation, which may be expressed in the general form

$$y = F(x, z, u, \dots),$$

presupposes the existence of physical magnitudes whose measurements are defined by the number symbols x, y, z, u, \dots , and a fundamental relation between the magnitudes which determines the form of the equation. Whether the magnitudes and this relation between them actually exist in the objective world is not important to the mathematician. He is more concerned with the transformations which it is possible for him to make in the equation, that is, with the equivalence of all possible groups of operations of measuring these magnitudes which he supposes to exist. He is quite justified, therefore, in creating in imagination a system of connected magnitudes in which his equations are true and which may be called a *world* or a *universe* but which would be different from the world of our experience and probably unintelligible to any one not a mathematician.

The physicist, however, by confining his magnitudes to those of the objective world, seeks for a correspondence between the form of his equation and the unknown connection between these magnitudes. He supposes that a certain connection between the magnitudes does exist which gives an assumed form to his equation and then, by a series of measurements upon the quantities involved, tests whether the numbers so obtained satisfy his assumed equation. In very few instances, in fact, is the confirmation really decisive, and the equation must be rejected altogether or only held as approximately resulting from the connection of the physical magnitudes with one another. But even if the equation is confirmed, it only shows how the measurement of one of the physical magnitudes depends upon the measurements of the others. It gives us no information as to what the connection really is or of the nature of the magnitudes themselves. Thus the form of the equation

$$a = b c$$

results equally from the connection that the area of a rectangle

has with its two bounding lines, that space has to velocity and time in the case of a moving body, or that work has to force and distance in the case of man's struggle with gravity.

A distinction must, therefore, be made between the real connection of physical magnitudes with one another and the corresponding equation between the numbers describing the ways by which these magnitudes are made up of their units. The nature of the former is as far beyond our knowledge as the nature of the force of gravitation; but the process of measuring these magnitudes and the use of symbolic numbers to describe the process, as well as the fact that this connection of the magnitudes results in an equation involving these numbers, is our own discovery, and quite within the circle of our knowledge. Nor does it seem possible that this mechanical process of measuring magnitudes, or any description of it, can materially add to our knowledge of the magnitudes themselves and their connections. That knowledge can come only by increasing the particular sense experiences of the magnitudes and their connections, and thus modifying the general notions we may have of them. The knowledge of how to measure these magnitudes is of great service to man in his efforts to adapt the objective world to his needs, but it is not absolutely necessary, for in his primitive state he lived and multiplied without that knowledge.

17. *Misconceptions Regarding Number.* It is true that there is a common idea that number itself possesses the property by which magnitudes are classified and is therefore a magnitude itself. This has arisen partly through confusion of ideas and syncopated language in early efforts to "learn" or memorize the multiplication and other symbolic tables of arithmetic, and partly through the law of association of ideas in attaching the properties of the magnitude itself to the symbol which defines the measurement of it, especially when the unit quantity is unexpressed by a word. In analyzing, however, the nature of the number concept it is essential that the concept of magnitude (conservation of identity during division into parts) be not attached to the language, words, or

symbols used to describe operations which we perform upon these magnitudes.

Thus after performing the necessary operations of measuring, we may say that AB is a centimetres and CD is b centimetres; but only the three things AB , CD , and the centimetre retain their distinguishing properties when they are divided into parts or repeated into wholes. The numbers a and b only describe the processes of measuring and are symbols of operation and not concepts of magnitude; and while it is commonly said that a is greater, or less, than b , just as we say that the line AB is greater, or less, than the line CD , it is understood that a only denotes a series of operations higher up, or lower down, in the conventionalized series of operations than b . Thus all numbers, algebraical or otherwise, are operators, or rather descriptions of operations, by which from some given unit magnitude another magnitude of the same kind may be formed.

18. *Summary and Conclusions.* From an analysis of the fundamental problem of construction it is seen that the elements upon which our conception of number is founded are not of the nature of the physical properties of magnitudes, but are discoverable in certain acts or operations which we perform upon these magnitudes. These elements include the primary processes of nature by which individual things were formed out of uniformity and the processes by which these things are arranged into classified groups. The number content of language consists of those words and symbols which enable us to describe these processes in terms of a fundamental but complex unit operation. This unit operation which all individuals by imitation have learned to perform is referred to and described by the number symbol "1". A system of number symbols then denotes and describes a conventionalized grouping of the unit operation in the process of constructing a required magnitude of any kind from the unit magnitude.

Arithmetical or algebraical identities describe two different ways of grouping the unit operation by which the same magnitude may be constructed from the same unit magnitude.

The fundamental relations or connections which physical magnitudes have to one another in an organized universe, either real or imagined, determine the form of the equations involving the measures of these magnitudes; but neither the nature of the magnitudes nor the nature of the connection between them may be inferred from the form of the equation.

The establishment of any hypothesis expressed by an equation can lead to truth only in respect to the measurements of physical magnitudes, and can furnish no information in regard to their actual or real nature and connection with one another. The truth concerning the latter can be only approximately obtained as generalizations from sense experiences.

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ARTICLE XV

THE POETRY OF MATHEMATICS

There are two kinds of mathematicians, and they have two ways of studying mathematics. The one regards all mathematical ideas as abstractions and the chief end to be attained the study of its symbolic language. The student of mere symbols becomes a calculating machine, incapable of sympathy with the thoughts and passions of ordinary men. He may pass among them as a profound thinker, but in reality he is dwelling near the borderland of insanity. The other regards all mathematical ideas as inseparable from the world of nature, and its language as an unerring guide which conducts him into new mysteries, and shows him beauties and harmonies he never dreamed of before. He is an artist and in complete accord with the world around him.

This is a world of beauty. Ever since our eyes opened on its wonders we have been beholding, comparing, contrasting, and grouping, often unconsciously, the natural things about us. The sky with its variegated hues, the restless sea, the solid mountains, the hazy valleys and the sunny plains, the verdant wood with its songs of birds, the murmuring stream, the sighing winds, and the majestic grandeur of a storm—all these are continually calling forth in us the latent sense of beauty. Sooner or later we form some sort of ideal, or standard, with which we compare all forms of beauty. If now on comparing some new object with this ideal we feel a sense of harmony, our artistic pleasure is great; and if, in addition, this ideal is enlarged and intensified, our pleasure is increased. But if, on the other hand, the object is not in harmony with, or degrades, our ideal, we turn away from it with a keen sense of pain.

In this ideal different forms of beauty may predominate. In ancient Greece it consisted largely of beauty of form, as evidenced in her sculpture and architecture. Her most beautiful columns have borrowed their curves from the hyperbola, and their colonnades obey a simple arithmetical

law. Later in history the elements of colour and sound entered into this ideal, and to-day they hold almost absolute sway. The one expresses itself in painting, the other in music. Yet the most elaborate and realistic painting would cause a sense of pain if the simple laws of mathematical perspective were violated, and the grandest strains of Mendelssohn or Mozart would crash in horrible discord were the mathematical laws of time and interval for an instant broken. But the poet's ideal incorporates all three elements of beauty. In his imagination are all beautiful forms, all sweet sounds, all harmonious colours. When the reader finds that these harmonize with and intensify his own ideals of beauty, and is captivated in addition by the very form and melody of the words themselves, he enters into the spirit of the poet, feels his rapture, and enjoys him to the full. For example, observe how Coleridge, in "The Ancient Mariner", appeals to all that is beautiful in our ideals and intensifies them by his own vision when he says:

Sweet sounds rose slowly through their mouths,
And from their bodies passed.

Around, around, flew each sweet sound,
Then darted to the sun;
Slowly the sounds came back again,
Now mixed, now one by one.

Sometimes a-dropping from the sky
I heard the skylark sing;
Sometimes all little birds that are,
How they seemed to fill the sea and air
With their sweet jargoning!

And now 'twas like all instruments,
Now like a lonely flute;
And now it is an angel's song,
That makes the heavens be mute.

It ceased; yet still the sails made on
A pleasant noise till noon,
A noise like of a hidden brook
In the leafy month of June,
That to the sleeping woods all night
Singeth a quiet tune.

But this implies on the part of the reader two things: First, the power to conceive an image in the mind, to hold it in view, to change it, or dismiss it at will; and secondly, the possession of a standard, or ideal, of beauty with the faculty of artistic judgment.

Our purpose is to show, that of all educated men the mathematician is qualified in an eminent degree to enjoy true poetry, and to distinguish it from that which is false, that he cannot read lines that strike the least note of discord, nor look upon an image whose form and setting lack the elements of true harmony.

Long, long ago among the classic hills of Greece there lived a strong and sturdy youth. His limbs were of such symmetrical mould that no one in all the world could match him in feats of strength or in the graceful movements of the body. His brow was of marble whiteness. His eyes were clear, and in them could be seen the light of a lofty purpose. The rest of his features were in keeping. He dwelt chiefly at Athens and Corinth, but frequently paid visits to his relatives in Alexandria and to his friends in other parts of the world. His delight was to consult and advise the workmen on the Pentelicus as they fashioned the stones for the temples and capitols which are the wonder of the succeeding ages. His attainments were great, yet he was ever restless, seeking after something or some one, he knew not what, feeling "cabin'd, cribb'd, confin'd," always striving after great things, accomplishing much, yet never reaching the full fruition of his powers.

All unknown to this youth, among the gentle slopes and sunlit hills of Spain a maiden was being reared with tender care. Day after day she played in the courts of those magnificent palaces reared by the worshippers of Mahomet as dwelling places for their princes. She was not strikingly beautiful. She had many friends, but few lovers. Oftentimes she sighed for some one worthy of her love, on whom she could rely. Years passed on, and this youth and maiden lived and longed, each unconscious of the existence of the other.

At length fell disaster overtook the maiden's parents and her people. Their lands were invaded, their palaces were sacked, and the maiden was forced to flee from her parental home to find a refuge in the cloisters of the Monastery. Thus it was that this noble Grecian youth, ever restless, himself driven from his native land, in his wanderings happened to meet the maiden. They felt strangely drawn to each other. The eyes of the youth glowed with a new light, and the face of the maiden shone with a new radiance. Thus their courtship began. Many an evening they spent together within the ivied walls of the Monastery as they talked to each other of their former lives and their new-found hopes. Strange place indeed for a courtship! The banns could not be published. They fled to Holland. There they were married. René Descartes performed the ceremony; and Geometry, the Grecian youth, and Algebra, the Moorish maiden, were forever united.

Thenceforth, happy in each other's love, they made their abode in the University of Europe, taking a perpetual pride in their offspring. From this union new families—nay, whole nations of families—were born into the mathematical world. Myriads of beautiful forms, most of them unlike anything seen by the natural eye, strange forms, yet all of them perfect, harmonious, and true! Not a single one out of keeping with the ideal of beauty! Not a blemish, not a discord, not an imperfection! The mathematical world is peopled full of these strangely beautiful forms, now fixed as the eternal hills, now changing, growing from one form to another, mingling together in endless variety; yet always there is regularity, perfection, and beauty.

The contemplation of these beautiful creatures of the imagination, which none but the mathematician can see, gives him a peculiar advantage over other men in forming a true ideal of beauty of form. Their very strangeness enlarges the scope of his imagination so that he may create other worlds as beautiful as that in which we live. Moreover, the clearness with which one may conceive a definite form, hold it in the mind, and contemplate its beauty,

comes from a close application to the study of geometry, and is in a great degree the measure of the reader's ability to enjoy the great imaginative poems. The door leading from the mathematician's gallery of beautiful forms into that of the poet's imagery is always open.

I said that from the union of these two lovers there sprang a generation of beautiful children. Here is one of them:

$$x=0. \dots\dots\dots (1)$$

It was my good fortune to spend my early days on the elevated banks on the north shore of Lake Erie. A few times on a summer evening you may have with me looked out on the water—not the slightest motion of the air, not a ripple on the pebbly beach, not the slightest undulation on the mirrored surface, which reflected the rays of the setting sun in a path of golden glory that seemed to carry our thoughts, nay, even our spirits, into another world as we stood entranced. But the earth is round, the surface dips, and our view is cut off. But suppose the surface did not dip, and the ancients were right in their view that the earth is flat, and the mirrored plane extends in one unbroken infinite level, in front, on either side, behind, forever. What if the Almighty had constructed the universe on this plan—all below dark and impenetrable—all above light and airy? Such a picture is called up in the mathematician's mind by the simple statement, $x=0$.

Here is another of their children:

$$x^2+y^2=kz^2. \dots\dots\dots (2)$$

The mathematical cone. A straight steel wire, of infinite length, and piercing a hole in the infinite plane, is made to slide rapidly against a circular ring held above and parallel with the plane. Look at the shape described.

Above the plane, a huge inverted mountain, perfect and beautiful in form, its point in the region where mortals live, its ever widening sides reaching beyond the faintest twinkling star. Its base cannot be conceived. Look at its counterpart below. Suppose the Creator had constructed the universe on this plan. The mighty cones, dark and solid earth;

the outside, light and airy. What thoughts teem in the imagination when we contemplate the possibility and the sublimity of such a universe! What people dwell there? What are their joys and their occupations? What geographical and astronomical discoveries have they made? What Newton has formulated a new law of attraction? What Shakespeare has touched the chords of new human passions? What Dante has imagined a still unseen world? I leave the wide field to others!

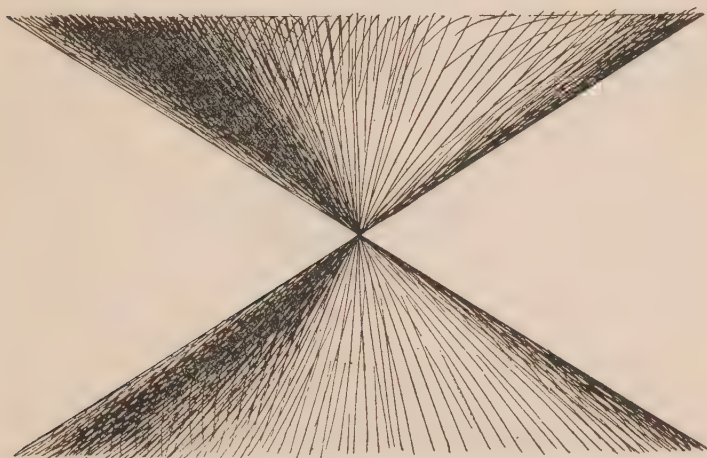


Figure 1.—Double Cone. Equation 2.

Referring to the equation,

$$x^2 + y^2 = kz^2,$$

by varying k we see the angle of the cone increase until the mighty slopes of its opposing parts approach each other, and clash in dire calamity.

Here I might suggest that, when the imagination is controlled by definite laws, the mind feels a peculiar pleasure in tracing out the delineations of its images, and gains vigour in doing so. In fact, these imaginary forms may become more real than the actual forms in this world. Without these controlling laws the images become hallucinations, and the mental powers are dissipated.

Again let us contemplate the beauty and the grandeur of the form called up by the equation,

$$x^2 + y^2 = n(z-a)(z-b)(z-c). \dots\dots\dots (3)$$

Its lower part consists of a huge mountain with endless gentle slopes, reaching forever outwards to join the infinite circle of the universe, its rounded top being situated in the region where mortals live. But what is that strange massive form, with swelling sides and flattened top, that hovers over the peak of the mountain, vertex answering to vertex? Strange and beautiful! The inexorable laws of mathematics will have it so. What if the Creator had constructed the universe after this plan, and mortals living there had guessed



Figure 2.—Illustrating Equation 3.

at the riddle of its existence as we have at that of our own, and had ceased to wonder at its strangeness? In the language of an ancient writer, I am led to say, "Such thoughts are too wonderful for me."

Now, let n increase and watch the swelling sides grow wider, while the slopes become more gentle. Next, let a grow into b , and behold the huge upper form vanish to a point, the sides of the mountain answering in graceful change. Finally, let b grow into c , and see the opposing vertices approach each other, pouting out their lips as they clasp their arms in one rapturous embrace.

The number and variety of these forms are only equalled

by the number of equations involving x , y , and z , which may be formed. Yet, perhaps, these examples will suffice to show that no branch of study furnishes so wide a field for the exercise of the imagination as that of mathematics. It develops, first, strength to conceive an image, and secondly, a taste for the beautiful in form. These two things constitute the essential conditions for the enjoyment of poetry. There are three elements of beauty, *sound*, *colour*, and *form*. "These three, but the greatest of these is" *form*.

Probably no writer appeals to the idea of form more than the poet Dante. He lived in an age when men thought the world was flat, and surrounded on all sides by an endless river. The habitable part of the flat world was the centre about which concentric heavenly spheres revolved within each other, one containing the moon, another the sun, others the planets, and still another the stars. There was another side to the flat world, but no mortal had ever seen it. Impious indeed would be he who should attempt to cross the endless stream and reach the unknown shores. Beneath the flat surface of the habitable world was one mighty inverted cone, within whose nine circles, ever narrowing down to the vertex, dwelt the lost spirits in the regions of eternal woe. We follow the poet and his guide in their perilous journey past the centre of the universe, where, having re-adjusted their equilibrium, they ascend by a new and unknown way to the regions of the opposite hemisphere and again behold the stars. I think the mathematician who has conceived the lower mountain form of the mathematical cone, will appreciate the vision that breaks upon their view when Dante says:

The dawn has chased the matin hour of prime,
Which fled before it, till, from afar,
I spied the trembling of the ocean's stream.

It is not my purpose to accompany the travellers in the unseen world as they climb the Mountain of Purgatory, but to point out that this mountain, easy of access towards the top, reaches to the entrance of Paradise. Unlike the Celestial

City in the Apocalypse, "which lieth four-square, and the length and the breadth and the height of it are equal", Dante's Paradise is an inverted cone, whose apex begins at the top of the Mountain of Purgatory, and whose sides, as they ascend, divide the concentric spheres of the moon, the sun, the planets, and the stars into regions where the immortal spirits of the dead, refined and purified on the Mountain of Purgatory, spend an endless existence in joys increasing as they ascend the circles of Paradise.

Sometimes the true appreciation of a poem depends not only on the clearness but on the rapidity with which the reader conceives the successive images. The necessary flexibility of the mind is greatly increased by studying the changing geometrical forms represented by equations containing variable and vanishing parameters. It is no trouble for the mathematician to leave the solid earth and identify himself with Shelley's cloud, and revel with delight among the images he sees.

That orbèd maiden with white fire laden,
Whom mortals call the Moon,
Glides glimmering o'er my fleece-like floor,
By the midnight breezes strewn;
And wherever the beat of her unseen feet,
Which only the angels hear,
May have broken the woof of my tent's thin roof,
The Stars peep behind her and peer;
And I laugh to see them whirl and flee,
Like a swarm of golden bees,
When I widen the rent in my wind-built tent,
Till the calm rivers, lakes, and seas,
Like strips of the sky fallen through me on high,
Are each paved with the moon and these.

Finally, the cultivation of the imagination, or image-forming power of the mind, is of great importance. It enables the teacher, the lecturer, and the public speaker to set his theme in a clear light. It lifts the mind out of the commonplace, and translates it into a new world. It strengthens one's faith in the reality of things not seen. It enriches the memory by many beautiful forms. It broadens our sympathy

and helps us to see things as others see them. We need to cultivate this image-forming power, because in this extremely practical and even skeptical age, we are apt to think that nothing is true unless it can be subjected to the "laboratory test", and brought within the range of our physical senses. We need to cultivate it, because it lifts the mind out of its narrow self, gives it a taste for that which is beautiful, and enables it to enter fully into that inheritance bequeathed us by the great and good men of the past—an inheritance not secured by title deeds, but free to all who will pay the price.

But there are other forms in the imaginary world which may not be reduced to a mathematical equation. One of these I have carried with me for a number of years. It is a small possession in the North of England, though I have not an exclusive right to its enjoyment. Originally it belonged to William Wordsworth:

I wandered lonely as a cloud
That floats on high o'er vales and hills,
When all at once I saw a crowd,
A host, of golden daffodils;
Beside the lake, beneath the trees,
Fluttering and dancing in the breeze.

Continuous as the stars that shine
And twinkle on the milky way,
They stretched in never-ending line
Along the margin of a bay:
Ten thousand saw I at a glance,
Tossing their heads in sprightly dance.

The waves beside them danced; but they
Out-did the sparkling waves in glee:
A poet could not but be gay,
In such a jocund company;
I gazed—and gazed—but little thought
What wealth the show to me had brought:

For oft, when on my couch I lie
In vacant or in pensive mood,
They flash upon that inward eye
Which is the bliss of solitude;
And then my heart with pleasure fills,
And dances with the daffodils.

"You have many beautiful things, and I have many beautiful things, but your beautiful things are not the same as my beautiful things," said a child to me.

"Indeed! and what are your beautiful things?"

"I do not like to tell you. If I tell you, you will say, pooh!"

On my assuring her that I would not, she replied, "My beautiful things are—babies and angels."

And I have kept my promise.

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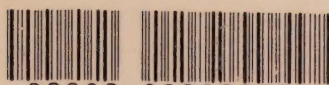


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